

2017

Resource recovery from wastewater using forward osmosis membranes

Ashley Joy Ansari

University of Wollongong, ashleyz@uow.edu.au

Follow this and additional works at: <https://ro.uow.edu.au/theses1>

University of Wollongong

Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

Recommended Citation

Ansari, Ashley Joy, Resource recovery from wastewater using forward osmosis membranes, Doctor of Philosophy thesis, School of Civil, Mining and Environmental Engineering, University of Wollongong, 2017. <https://ro.uow.edu.au/theses1/156>

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au



UNIVERSITY
OF WOLLONGONG
AUSTRALIA

School of Civil, Mining and Environmental Engineering
Faculty of Engineering and Information Sciences

RESOURCE RECOVERY FROM WASTEWATER USING FORWARD OSMOSIS MEMBRANES

A thesis submitted in the fulfilment of the requirements for
the award of the degree of

Doctor of Philosophy

from

University of Wollongong

by

Ashley Joy Ansari

September 2017

DECLARATION

This declaration is to certify that the work presented in this thesis was completed by the author, unless specified otherwise, and that no part of it has been submitted in a thesis to any other university or institution.

This thesis was prepared in the compilation style format and is based on the published journal articles listed in Thesis Related Publications. The citation and status of each journal article are also shown at the beginning of each chapter. All related journal articles were conducted and written during the author's candidature. Despite a certain level of repetition between chapters in introductory material and analytic methods, each single chapter was substantially different in focus and content within the scope of the thesis theme.

Ashley J. Ansari

September 2017

Dedication

This thesis is dedicated to the loving memory of my grandmother, Joyce Breeze, who was always there beside me. Thank you for your inspiration and unfaltering support.

THESIS RELATED PUBLICATIONS

Peer-reviewed Journal Articles

1. **A.J. Ansari**, F.I. Hai, W. Guo, H.H. Ngo, W.E. Price and L.D. Nghiem, Selection of forward osmosis draw solutes for subsequent integration with anaerobic treatment to facilitate resource recovery from wastewater, *Bioresource Technology*, 191 (2015), 30-36.
2. **A.J. Ansari**, F.I. Hai, W. Guo, H.H. Ngo, W.E. Price and L.D. Nghiem, Factors governing the pre-concentration of wastewater using forward osmosis for subsequent resource recovery, *Science of the Total Environment*, 566-567 (2016), 559-566.
3. **A.J. Ansari**, F.I. Hai, W.E. Price and L.D. Nghiem, Phosphorus recovery from digested sludge centrate using seawater-driven forward osmosis, *Separation and Purification Technology*, 163 (2016), 1-7.
4. **A.J. Ansari**, F.I. Hai, W.E. Price, J.E. Drewes and L.D. Nghiem, Forward osmosis as a platform for resource recovery from municipal wastewater - A critical assessment of the literature, *Journal of Membrane Science*, 529 (2017), 195-206.
5. **A.J. Ansari**, F.I. Hai, T. He, W.E. Price and L.D. Nghiem, Physical cleaning techniques to control fouling during the pre-concentration of high suspended solid content solutions by forward osmosis, Submitted to *Desalination* on 29.06.2017 (under review).

Conference Presentation

1. **A.J. Ansari**, W.E. Price, and L.D. Nghiem, Selection of forward osmosis draw solutes for subsequent integration with anaerobic treatment to facilitate resource recovery from wastewater. Oral presentation at the *4th IWA Regional Conference on Membrane Technology, Ho Chi Minh, Vietnam, 3rd – 6th December 2014*.
2. **A.J. Ansari**, F.I. Hai, W.E. Price, and L.D. Nghiem, Factors affecting forward osmosis membrane performance during wastewater pre-concentration. Oral presentation at the *2nd NU Membrane Workshop in Australia, Sydney, Australia, 13th November 2015*.
3. **A.J. Ansari**, F.I. Hai, W.E. Price, and L.D. Nghiem, Integrating FO with anaerobic treatment for simultaneous wastewater treatment and resource recovery – process performance and challenges. Oral presentation at the *9th International Membrane Science and Technology Conference (IMTSEC), Adelaide, Australia, 5th – 8th December 2016*.

ACKNOWLEDGEMENTS

I would like to first thank my supervisor, Long Nghiem, for his continuous support throughout my university studies. I feel extremely lucky to have a supervisor who is patient, caring, encouraging, and wise. His guidance has been invaluable to me and I hold a strong appreciation for his work ethic, research approach, and enthusiasm.

This gratitude also extends to my co-supervisors, Faisal Hai and Will Price who always provided valuable inputs during my PhD.

Completing this thesis would have been all the more difficult were it not for the support and friendship provided by the members of our research group. Special thanks to Hung, Kaushi, and Ricky for bringing excitement into our office. Also, thanks to the team; Lewa, Luong, Richard, Tabea, Wenhai, Sherry, Aileen, Sultan, Hop, Lei, Sihuang, Bilal, Minh, and Allie for the fun memories and motivation. My greatest thanks are expressed to my husband, Mark, and my family for always showing love and support.

Many thanks to the Technical Staff at the University of Wollongong, particularly, Linda, Frank, and Ritchie, for their help in the lab. I would also like to thank the team at Sydney Water's Wollongong Water Recycling Plant for their support during the many sampling visits.

Finally, I would like to acknowledge that this research has been conducted with the support of the Australian Government Research Training Program Scholarship. I also gratefully acknowledge the scholarship support by the University of Wollongong.

ABSTRACT

Forward osmosis (FO) is an emerging membrane separation technology that has the potential to serve as a game changer in wastewater treatment. FO-based processes can simultaneously produce high quality effluent and pre-concentrate wastewater for anaerobic treatment to facilitate the recovery of energy and nutrients. Complex wastewaters can be directly pre-treated by FO, and fresh water can be produced when FO is coupled with a draw solute recovery process (i.e. reverse osmosis or membrane distillation). By enriching organic carbon and nutrients for subsequent biogas production, FO extends the resource recovery potential of current wastewater treatment processes. Despite this potential, FO research is still in its infancy, and applications of FO for simultaneous treatment and resource recovery from municipal wastewater are developing. This thesis focuses on investigating and optimising the use of FO membranes for resource recovery applications, with respect to, integrating FO with anaerobic treatment, draw solute selection, mitigating salinity build-up, and membrane fouling.

A selection protocol was developed to determine suitable draw solutes for FO membrane systems that integrate anaerobic treatment for biogas recovery. Draw solutes were evaluated in terms of their ability to induce osmotic pressure, water flux, and reverse solute flux. The compatibility of each draw solute with subsequent anaerobic treatment was assessed by biomethane potential (BMP) analysis. Ten draw solutes were evaluated at the same osmotic pressure (i.e. 30 bar) and each draw solute exhibited diverse flux performance. The results showed a strong influence of draw solute physiochemical properties on water and reverse solute flux. This correlation suggested that a trade-off exists between the selection of highly diffusive draw solutes that display high water flux, and those which show a low reverse solute flux. Sodium acetate (NaOAc) and magnesium acetate (Mg₂OAc) displayed unique behaviour compared to other draw solutes, as a high water flux and reverse solute flux selectivity was achieved. BMP analysis indicated that ionic organic draw solutes (e.g., NaOAc and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na)) were most suitable when integrating FO with anaerobic treatment. On the other hand, the reverse solute flux of inorganic draw solutions (e.g. sodium chloride (NaCl)) appeared to inhibit methane production by 11% in FO pre-concentrated wastewater at the concentration corresponding to a ten-fold concentration factor.

The key factors governing the FO process during wastewater pre-concentration were investigated using a lab-scale system. The selected draw solution, system concentration factor, and operational conditions were studied based on the effects on organic matter and nutrient retention, salinity accumulation, and membrane fouling. The chemical oxygen demand (COD) of raw wastewater was concentrated up to approximately eight-fold at a water recovery of 90%. Thus, even low strength wastewater could be pre-concentrated by FO to the range suitable for biogas production via anaerobic treatment. Excessive salinity accumulation in pre-concentrated wastewater was successfully mitigated by adopting ionic organic draw solutes, namely, NaOAc, and EDTA-2Na. Significant membrane fouling was observed when operating at 90% water recovery using raw wastewater. Nevertheless, membrane fouling was reversible and was effectively controlled by optimising the hydrodynamic conditions of the cross-flow FO system during the short-term experiment cycles.

Raw wastewater and digested sludge centrate can be filtered using FO to recover organic matter and nutrients. The fouling propensity of digested sludge centrate, and the effectiveness of membrane flushing, air-scouring, and ultrasonication for physical cleaning were systematically evaluated. Accelerated fouling conditions were applied to simulate the long-term and intensive pre-concentration scenario that is required for phosphorus recovery from digested sludge centrate. The results suggest that membrane fouling during forward osmosis operation to pre-concentrate digested sludge centrate is mostly due to the deposition of small mineral crystals and particulate matter on the membrane surface. Both high cross-flow velocity flushing and ultrasonication were effective at preventing membrane fouling under accelerated fouling conditions. The results also highlight the potential of intermittent membrane cleaning for achieving a higher cumulative permeate volume and lower energy consumption in comparison to continuous application to prevent membrane fouling. Among several physical cleaning regimes investigated in this chapter, the combination of ultrasonication and high cross-flow velocity flushing was the most effective and could maintain stable FO operation over several repetitive cleaning cycles.

Integrating FO with anaerobic treatment is a necessary step to develop low impact wastewater treatment systems. The performance of this process was demonstrated using a lab-scale FO system equipped with a polyamide thin film composite (TFC) membrane, as well as using BMP analysis as an indication of anaerobic treatment efficiency. The FO concentration factor (i.e. system water recovery) was optimised in terms of maximising organic content as well as by limiting salinity accumulation in pre-concentrated wastewater.

Lower salinity accumulation was achieved by using NaOAc as the draw solute. Additionally, the effect of FO concentration factor on anaerobic performance was elucidated by experimentally evaluating the methane production at various simulated FO concentration factors. For NaCl and NaOAc, the cumulative methane production increased as the system water recovery was maximised (i.e. up to 90%). At a water recovery value of 50% and 80%, the methane production of NaCl and NaOAc exhibited a similar behaviour, due to the marginal differences in pre-concentrated wastewater characteristics. However, for 90% water recovery, NaOAc tended to produce a larger and more consistent amount of methane compared with NaCl, due to the higher contribution of degradable reverse solute flux. Thus, in terms of wastewater pre-concentrate digestibility, no critical concentration factor was found for both draw solutes under these conditions (i.e. 90% water recovery and inoculum/substrate ratio of 2:1). Although FO reverse solute flux has the potential to negatively affect anaerobic treatment, careful selection of FO operating parameters and digester loadings can clearly improve the process performance. The results also show that the rate of membrane fouling on the TFC membrane was higher compared with the cellulose triacetate (CTA) membrane used in other chapters of this thesis, due to the significantly larger initial water flux of the TFC membrane. Despite this, the full recovery of the water flux after physically flushing the TFC membrane indicated that no irreversible fouling occurred and that it was limited to surface deposition. The results confirm that TFC membranes have a number of notable advantages for wastewater pre-concentration.

Phosphorus recovery from wastewater is essential for the development of resource recovery practices, however, high cost processes limit the feasibility of widespread application. Here, a novel seawater-driven FO process to recover calcium phosphate precipitates from digested sludge centrate without any chemical addition or draw solute regeneration was proposed. The FO process effectively pre-concentrated phosphate and calcium in the digested sludge centrate. Spontaneous precipitation of calcium phosphate minerals in the digested sludge centrate was achieved by the sustained concentrative action of the FO process and the gradual pH increase due to the diffusion of protons to the draw solution. Pre-concentrating digested sludge centrate by three-fold resulted in a 92% recovery of phosphate via precipitation. The phosphate precipitate only constituted 3% of the total solids recovered, therefore subsequent treatment steps would be required to recover phosphorus in a useable form. A water flux decline of 30% from the initial value was observed as the digested sludge centrate was concentrated by three-fold. This observed water

flux decline was mostly attributed to the decrease in the effective osmotic driving force due to the increasingly concentrated feed solution and diluted draw solution. It is also noteworthy that membrane fouling was readily reversible within the single concentration cycle. By flushing the membrane with deionised water and subjecting the membrane to feed and draw solutions with the same osmotic pressure as the initial conditions, complete water flux recovery could be achieved.

TABLE OF CONTENTS

DECLARATION	I
THESIS RELATED PUBLICATIONS	III
ACKNOWLEDGEMENTS	IV
ABSTRACT	V
TABLE OF CONTENTS	I
LIST OF FIGURES	V
LIST OF TABLES	XI
CHAPTER 1: INTRODUCTION	1
1.1. Background	1
1.1.1. Water – energy – nutrient nexus	2
1.1.2. Wastewater treatment to resource recovery	4
1.2. Integrated resource recovery	6
1.2.1. Water recovery	6
1.2.2. Energy recovery	7
1.2.3. Nutrient recovery	8
1.3. Strategies to maximise the recovery of resources	10
1.3.1. Source separation	10
1.3.2. Co-digestion	10
1.3.3. Pre-concentration	10
1.4. Pre-concentration opportunities at wastewater treatment plants	11
1.5. Objectives and thesis scope	12
1.6. Thesis outline	13
CHAPTER 2: FORWARD OSMOSIS AS A PLATFORM FOR RESOURCE RECOVERY FROM MUNICIPAL WASTEWATER – A CRITICAL ASSESSMENT OF THE LITERATURE	15
2.1. Introduction	15
2.2. Forward osmosis	17
2.2.1. Forward osmosis membranes	18
2.2.2. Configurations	20
2.2.3. Draw solutes	20
2.2.4. Concentration polarisation	21
2.2.5. Reverse solute flux	22

2.2.6.	Membrane fouling.....	22
2.2.7.	Draw solute regeneration and water recovery processes	23
2.3.	Forward osmosis for wastewater treatment	24
2.3.1.	Forward osmosis system configurations for wastewater treatment	25
2.3.2.	Treatment performance of forward osmosis systems	27
2.3.3.	Forward osmosis membrane-based hybrid systems for water recovery	29
2.4.	Resource recovery using forward osmosis	33
2.4.1.	Integrating forward osmosis with anaerobic treatment for biogas production	34
2.4.2.	Nutrient recovery	41
2.5.	Integrated wastewater treatment and resource recovery process	44
2.6.	Outlook	46
2.7.	Conclusion	47
CHAPTER 3: SELECTION OF FORWARD OSMOSIS DRAW SOLUTES FOR SUBSEQUENT INTEGRATION WITH ANAEROBIC TREATMENT TO FACILITATE RESOURCE RECOVERY FROM WASTEWATER.....		49
3.1.	Introduction.....	49
3.2.	Materials and methods	51
3.2.1.	Preliminary draw solution selection protocol	51
3.2.2.	Materials and chemicals.....	51
3.2.3.	Forward osmosis system.....	51
3.2.4.	Forward osmosis assessment	52
3.2.5.	Biomethane potential apparatus and protocol.....	53
3.2.6.	Analytical methods	55
3.3.	Results and discussion	55
3.3.1.	Preliminary draw solution selection.....	55
3.3.2.	Forward osmosis flux performance	56
3.3.3.	Effect of reverse draw solute flux on anaerobic treatment	60
3.3.4.	Draw solute suitability for anaerobic treatment.....	62
3.4.	Conclusions.....	63
CHAPTER 4: FACTORS GOVERNING THE PRE-CONCENTRATION OF WASTEWATER USING FORWARD OSMOSIS FOR SUBSEQUENT RESOURCE RECOVERY		64
4.1.	Introduction.....	64
4.2.	Materials and methods	67

4.2.1.	Materials and chemicals.....	67
4.2.2.	Forward osmosis system.....	67
4.2.3.	Experimental protocol.....	68
4.2.4.	Analytical methods	69
4.3.	Results and discussion	69
4.3.1.	Forward osmosis pre-concentration of organic matter in wastewater	69
4.3.2.	Ionic organic draw solutes for wastewater pre-concentration	72
4.3.3.	Membrane fouling.....	78
4.3.4.	Fouling reversibility and water flux sustainability	79
4.4.	Conclusions.....	80
CHAPTER 5: PHYSICAL CLEANING TECHNIQUES TO CONTROL FOULING DURING THE PRE-CONCENTRATION OF HIGH SUSPENDED SOLID CONTENT SOLUTIONS BY FORWARD OSMOSIS		81
5.1.	Introduction.....	81
5.2.	Materials and methods	83
5.2.1.	Materials and chemicals.....	83
5.2.2.	Forward osmosis system.....	83
5.2.3.	Cleaning Equipment.....	84
5.2.4.	Accelerated fouling experimental protocol.....	85
5.2.5.	Physical cleaning	86
5.2.6.	Membrane autopsy.....	86
5.2.7.	Analytical methods	86
5.3.	Results and discussion	87
5.3.1.	Fouling propensity of wastewater and digested sludge centrate.....	87
5.3.2.	Membrane fouling prevention.....	89
5.3.3.	Membrane cleaning.....	92
5.4.	Conclusions.....	98
CHAPTER 6: INTEGRATING FORWARD OSMOSIS WITH ANAEROBIC TREATMENT FOR SIMULTANEOUS WASTEWATER TREATMENT AND RESOURCE RECOVERY: PROCESS PERFORMANCE AND CHALLENGES		99
6.1.	Introduction.....	99
6.2.	Materials and methods	101
6.2.1.	Materials and chemicals.....	101
6.2.2.	Forward osmosis system.....	102

6.2.3.	Biochemical methane potential experimental set-up	103
6.2.4.	Experimental protocol.....	103
6.2.5.	Analytical methods	104
6.3.	Results and discussion	104
6.3.1.	Pre-concentration performance using thin film composite membrane	104
6.3.2.	Effect of forward osmosis concentration factor on methane production	106
6.3.3.	Water flux decline and flux recoverability	110
6.4.	Conclusions.....	110
CHAPTER 7: PHOSPHORUS RECOVERY FROM DIGESTED SLUDGE CENTRATE USING SEAWATER-DRIVEN FORWARD OSMOSIS.....		112
7.1.	Introduction.....	112
7.2.	Materials and methods	115
7.2.1.	Forward osmosis system	115
7.2.2.	Experimental protocol.....	115
7.2.3.	Analytical methods	116
7.2.4.	Digested sludge centrate and seawater	117
7.2.5.	Forward osmosis water flux model.....	117
7.2.6.	Mineral species estimation.....	118
7.3.	Results and discussion	119
7.3.1.	Forward osmosis membrane nutrient rejection.....	119
7.3.2.	Phosphorus removal and recovery	121
7.3.3.	Membrane fouling and water flux dynamics	124
7.3.4.	Implications.....	125
7.4.	Conclusions.....	126
CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK ..		127
8.1.	Conclusions.....	127
8.2.	Recommendations for future work	130
REFERENCES		131

LIST OF FIGURES

Figure 1.1. The water – energy – nutrient nexus for resource recovery from wastewater.	3
Figure 1.2. Resource content and relative economic value of municipal wastewater [18].	5
Figure 1.3. Current and achievable targets for chemical energy generation to meet the requirements of wastewater treatment processes, including; conventional activated sludge (CAS), membrane bioreactor (MBR), and reverse osmosis (RO) [23]......	7
Figure 1.4. Pre-concentration based flow sheet for integrated resource recovery. Pre-concentration processes enable water and nutrient recovery, whilst energy is produced from anaerobic digestion, utilising a combined heat and power (CHP) system.	12
Figure 1.5. Thesis outline.....	14
Figure 2.1. Cross-sectional SEM images of (A) CTA FO membrane – polyester mesh embedded within the polymer material and (B) TFC FO membrane – polyamide with PET non-woven fabric support. Figure adapted from Cath, et al. [69] and Yip, et al. [70]......	19
Figure 2.2. Concentration profile for asymmetric FO membrane (FO mode) demonstrating external concentration polarisation (ECP) of the feed and draw solutions; and internal concentration polarisation (ICP) within the support layer.	21
Figure 2.3. Schematic representation of three major FO system configurations for wastewater treatment: (A) Ae-OMBR, (B) An-OMBR, and (C) wastewater pre-concentration intended for subsequent anaerobic digestion.	26
Figure 2.4. Schematic of FO membrane-based hybrid systems utilising: (A) pressure driven RO or NF, (B) thermally driven MD, and (C) electrically driven ED.....	30
Figure 2.5. Schematic of an FO pre-concentration process for energy recovery via anaerobic treatment.	36
Figure 2.6. Mitigation of salinity accumulation by (A) alternative draw solutions for Ae-OMBR [134] and (B) MF withdrawal of total dissolved solids (TDS) in an OMBR (adapted from Qiu et al. [151]).	38

Figure 2.7. Phosphorus recovery using (A) MF withdrawal from Ae-OMBR mixed liquor (adapted from Qiu et al. [151]) and (B) FO-MD of anaerobically digested sludge centrate (adapted from Xie et al. [152]).	43
Figure 2.8. Comparison of current and FO-based wastewater treatment technologies. (A) Current processes consume significant energy, dissipate wastewater organic matter, and do not effectively manage nutrients (adapted from Verstraete et al. [45]). (B) The proposed FO-based treatment process achieves simultaneous wastewater treatment and resource recovery, utilising produced energy within its operations and recovering nutrients.	45
Figure 3.1. Schematic diagram of the laboratory-scale FO system.	52
Figure 3.2. (A) Schematic diagram and (B) photo of the biochemical methane potential (BMP) set-up.	54
Figure 3.3. Average water flux, reverse solute flux and reverse solute flux selectivity (RSFS) at an osmotic pressure of 30 bar. Error bars represent the standard deviation of duplicate experiments.	57
Figure 3.4: Relationship between diffusion coefficient and (A) water flux (linear regression $R^2 = 0.90$); (B) reverse solute flux (exponential regression $R^2 = 0.81$). Experiments were conducted at constant osmotic pressure (30 bar); error bars represent the standard deviation of duplicate experiments.	58
Figure 3.5. Variation of water flux with reverse solute flux selectivity (RSFS) to compare sodium acetate and magnesium acetate with other draw solutions (DS). Experiments were conducted at constant osmotic pressure (30 bar); error bars represent the standard deviation of duplicate experiments.	59
Figure 3.6. Cumulative methane production of digested sludge with dosed draw solute at concentrations corresponding to FO RSFS and 90% system recovery; error bars represent the standard deviation of duplicate experiments.	61
Figure 4.1. Graphical representation of the challenges and potential solutions relating to wastewater pre-concentration using the FO process.	66
Figure 4.2. (A) Initial and final (i.e. at water recovery of 90%) COD concentrations for low and moderate strength wastewater. Error bars represent the standard deviation of triplicate COD sample measurements. (B) Variation of experimental and calculated	

wastewater COD concentration factor during FO pre-concentration. Error bars represent the standard deviation of triplicate COD sample measurements from duplicate experiments. The initial wastewater COD for low and moderate strength wastewater were 137 ± 8 mg/L, and 356 ± 13 mg/L, respectively. Mass balance assumes 100% COD retention in feed solution. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar, NaCl draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s).....70

Figure 4.3. (A) Variation of wastewater conductivity during wastewater pre-concentration for sodium chloride, sodium acetate, and EDTA-2Na. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s). The initial wastewater conductivity was 1.05 ± 0.02 mS/cm. (B) Water flux, reverse solute flux, and reverse solute flux selectivity (RSFS) of sodium chloride, sodium acetate, and EDTA-2Na. Experimental conditions: as above, with DI water feed solution (4 L). Error bars represent the standard deviation of measurements from duplicate experiments.73

Figure 4.4. Ionic organic draw solution binary ion diffusion analysis with linear regressions. (A) Sodium acetate and (B) EDTA-2Na. Experimental conditions: As in Figure 4.3B.74

Figure 4.5. Variation of COD concentration during wastewater pre-concentration for (A) low strength and (B) moderate strength wastewater. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s). Error bars represent the standard deviation of triplicate COD measurements..75

Figure 4.6. Water flux decline during batch wastewater pre-concentration. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s).76

Figure 4.7. Variation of pre-concentrated wastewater pH during batch wastewater pre-concentration experiments. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar draw solution; cross-flow rates of both feed and draw solutions were 1

L/min (corresponding to a cross-flow velocity of 16.7 cm/s). Error bars represent the standard deviation of measurements from duplicate experiments.	77
Figure 4.8. Effect of applied cross-flow velocity on water flux during the continuous flow experiment. Experimental conditions: primary effluent feed solution (5 L); $\pi = 60$ bar, NaCl draw solution; cross-flow rates of both feed and draw solutions were adjusted to achieve desired cross-flow velocity.	78
Figure 4.9. Variation of water flux during the continuous flow experiment for one pre-concentration cycle and at a fixed 90% water recovery (i.e. Rec = 90%). Experimental conditions: primary effluent feed solution (5 L); $\pi = 60$ bar, NaCl draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s).....	79
Figure 5.1. Schematic representation of an FO system with (A) air-scouring and (B) ultrasonication cleaning equipment.	85
Figure 5.2. Comparison of wastewater and digested sludge centrate fouling propensity. Fouling propensity is represented as the observed water flux decline during accelerated fouling conditions. Initial water flux of wastewater and digested sludge centrate was 20.0 ± 0.5 L/m ² h. Accelerated fouling conditions: feed solution was either wastewater or digested sludge centrate; NaCl draw solution was maintained at 3 M; cross-flow rates of both the feed and draw solutions were 0.5 L/min (corresponding to a cross-flow velocity of 8.3 cm/s).	87
Figure 5.3. (A) SEM micrograph and (B) EDS spectra of the FO membrane surface at the conclusion of the accelerated fouling experiment using digested sludge centrate as the feed solution. Experimental conditions are described in Figure 5.2.....	89
Figure 5.4. Normalised water flux decline during accelerated fouling conditions with; (A) 5x cross-flow velocity (i.e. 42 cm/s), (B) air-scouring, and (C) ultrasonic application, applied as fouling prevention techniques. Prevention techniques were continuously applied during the filtration time. Reference condition represents fouling cycle under accelerated fouling conditions. Accelerated fouling conditions: feed solution was digested sludge centrate; NaCl draw solution was maintained at 3 M; cross-flow rates of both the feed and draw solutions were 0.5 L/min (corresponding to a cross-flow velocity of 8.3 cm/s).	91

Figure 5.5. Water flux decline profile for a single digested sludge centrate fouling cycles using 30 minutes in-situ high cross-flow velocity flushing (i.e. 42 cm/s) with DI water. Accelerated fouling conditions: feed solution was digested sludge centrate; NaCl draw solution was maintained at 3 M; cross-flow rates of both the feed and draw solutions were 0.5 L/min (corresponding to a cross-flow velocity of 8.3 cm/s).	93
Figure 5.6. Water flux decline profile for repetitive, digested sludge centrate accelerated fouling cycles using 30 minutes in-situ high cross-flow velocity flushing (i.e. 42 cm/s) with DI water. Experimental conditions are as in Figure 5.5.	93
Figure 5.7. Accelerated fouling profile and water flux recovery after applying 30 minutes of (A) low cross-flow velocity (CFV), (B) high cross-flow velocity, (C) ultrasonic application with low cross-flow velocity, and (D) ultrasonic application with high cross-flow velocity. Experimental conditions are as in Figure 5.5.....	95
Figure 5.8. Water flux decline profile for repetitive, digested sludge centrate accelerated fouling cycles using 30 minutes in-situ high cross-flow velocity flushing (i.e. 42 cm/s) and ultrasonic application with DI water. Experimental conditions are as in Figure 5.5.....	96
Figure 5.9. SEM micrographs and EDS spectra of the (A) pristine FO membrane, (B) fouled membrane, and (C) membrane after ultrasonic assisted flushing cleaning. Experimental conditions are described in Figure 5.8.....	97
Figure 6.1. Pre-concentration of wastewater COD using NaCl draw solution and TFC FO membrane. Experimental conditions: primary effluent feed solution (2 L); $\pi = 30$ bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s).	105
Figure 6.2. Variation in wastewater conductivity for NaCl and NaOAc draw solutions. Experimental conditions as in Figure 6.1.	106
Figure 6.3. Average cumulative methane production over the 30 day evaluation period at various wastewater (WW) pre-concentration stages using (A) NaCl and (B) NaOAc FO draw solutions. Error bars represent n=4 measurements, with two BMP experiments and each condition being performed in duplicate.	108
Figure 6.4. Total methane production indicating no critical concentration factor existed up to 90% water recovery. Experimental conditions as in Figure 6.3.	109

Figure 6.5. Water flux decline and recoverability during FO pre-concentration using TFC membrane. Membrane flushing was performed for 30 min using DI water as the feed and draw solution at double the experimental cross-flow velocity). Experimental conditions as in Figure 6.2. Experimental duration is equivalent to 65 and 72 hours for NaCl and NaOAc, respectively.....	110
Figure 7.1. Variation of feed solution (FS) and draw solution (DS) concentration, and FO membrane rejection of (A) PO_4^{3-} , (B) Ca^{2+} , (C) Mg^{2+} , and (D) K^+ during FO treatment of digested sludge centrate. The red solid lines ($C_{\text{Ca,DS}}$, $C_{\text{Mg,DS}}$, and $C_{\text{K,DS}}$) are the calculated Ca^{2+} , Mg^{2+} , and K^+ concentration in the draw solution, respectively. All calculations assume that the FO membrane retains 100% of Ca^{2+} , Mg^{2+} , and K^+	119
Figure 7.2. Variation of sludge centrate pH and the mass of PO_4^{3-} , Ca^{2+} , and Mg^{2+} in the feed solution during FO treatment of digested sludge centrate.	121
Figure 7.3. Indicative PO_4^{3-} removal by precipitation from digested sludge centrate during seawater-driven FO.....	122
Figure 7.4. (A) Scanning electron microscopic image, (B) energy dispersive X-ray spectrometry spectrum, and (C) elementary composition of the recovered solids (ICP-OES measurement of the precipitate dissolved in acid).	123
Figure 7.5. (A) Simulated variation of feed solution (FS) and draw solution (DS) osmotic pressure resulting in the reduction of the osmotic driving force during closed-loop FO filtration (FS:DS volume = 3:10 L). (B) Simulated and experimental relative flux decline, with flux recoverability after membrane flushing and after replacing the feed and draw solutions. The experimental water flux was initially 6.4 L/m ² h.	124

LIST OF TABLES

Table 2.1. Summary of FO wastewater treatment performance in terms of the removal efficiency of organic matter (i.e. total organic carbon (TOC) and chemical oxygen demand (COD)), phosphorus (i.e. total phosphorus (TP)), and nitrogen (i.e. $\text{NH}_4^+\text{-N}$ and total nitrogen (TN)).	28
Table 2.2. Summary of FO-based resource recovery processes.	35
Table 3.1. Molar concentration required to generate 30 bar of osmotic pressure and solute diffusion coefficients. Concentrations were calculated using OLI Stream Analyzer.	56
Table 3.2. Expected draw solute concentration (by reverse solute flux) in pre-concentrated wastewater assuming 90% FO system water recovery.	59
Table 3.3. Substrate characterisation for BMP experiments (average concentration \pm standard deviation from duplicate measurements).	61
Table 5.1. Characteristics of raw wastewater and digested sludge centrate (average concentration \pm standard deviation from triplicate measurements). The minimum FO rejection was calculated based on experimental data from our previous study [200].	88
Table 6.1. Characterisation of real wastewater for the FO feed solution (average concentration \pm standard deviation from triplicate measurements).	101
Table 6.2. Variation in wastewater conductivity and COD simulated in BMP experiments for NaCl and NaOAc. The calculated total COD in each BMP bottle is also shown. Two BMP experiments were performed and each condition was conducted in duplicate.	107
Table 7.1: Key physicochemical properties of digested sludge centrate feed solution (FS) and seawater draw solution (DS) (average \pm standard deviation from triplicate measurements).	117

CHAPTER 1: Introduction

1.1. Background

Water scarcity and wastewater management are two closely related global issues with increasing contemporary and future importance. Depletion of fresh water sources by a growing population and the difficulties associated with safe wastewater management represent challenges towards human health and contamination of the environment. Water scarcity has driven the utilisation of alternative and often- unconventional water sources to preserve and augment potable fresh water supplies. In some areas, unconventional water sources such as seawater or wastewater have become a prominent source of potable water supply due to limiting factors such as climate, geography, and increasing fresh water demand [1, 2].

The motivation for wastewater treatment plants (WWTPs) to recover high quality water from wastewater has also been driven by a number of other reasons. Recognition of the devastating implications of discharging untreated or inadequately treated wastewater into the environment has led most governments to set stringent regulations to control the quantity and quality of effluent. Effluent quality guidelines are often based on the sensitivity of the receiving environment, however, improved treatment technology has also allowed for more progressive and stringent effluent quality regulations [3-5]. As a result, the production of high quality product water from wastewater is highly energy and resource intensive, with large associated capital and operational costs. Water reclamation has become an integral function of modern WWTPs and is becoming a widely adopted practice [6].

The environmental and financial cost of the energy and resources required to produce high quality water from wastewater has ironically resulted in the questioning of the sustainability of WWTPs [7]. A growing concern involves the energy consumption of wastewater operations, which has correspondingly increased with the introduction of advanced treatment processes and therefore effluent quality. Low energy, high performance treatment technologies are expected to play a pivotal role in future wastewater treatment sustainability, as well as the utilisation of available renewable energy sources. Much like the benefits which have been realised by recovering water from wastewater, further opportunities exist for other resources found in wastewater. Wastewater predominantly contains water, chemical energy, and nutrients. Water recovery is well established, however, a greater focus

is required to advance processes to more efficiently recover energy and nutrients from wastewater. The chemical energy in wastewater can be anaerobically digested to produce methane rich biogas, to offset the energy requirements of treatment operations. In addition, nutrients often form the focus of effluent water quality regulations, and therefore the effort spent trying to reduce their concentrations to acceptable levels, may be better utilised in recovering them.

One major limitation that restricts the practical recovery of energy and nutrients from wastewater is the relatively low concentration of organic compounds (for energy recovery) and even lower concentration of nitrogen and phosphorus (for nutrient recovery) in raw wastewater. Despite the existence of adequate recovery techniques, these practices have been rarely adopted, because of the inadequate concentrations in wastewater to allow feasible recovery. Additional drivers to improve energy and nutrient recovery from wastewater include the global demands for consistent renewable energy sources as well as the need for a sustainable and reliable phosphorus supply for fertilizer production. These aspects therefore provide a strong incentive to practice energy and nutrient recovery. There are however a number of existing technological limitations to overcome.

1.1.1. Water – energy – nutrient nexus

Water, energy, and food security are inextricably linked. Basic human rights and the precursors for socioeconomic development include access to safe drinking water and sanitation; clean, reliable and affordable energy services; and safe and nutritious food [8]. Figure 1.1 highlights the nexus between water, energy, and nutrients, with water resources playing an integral role in their security. A secure water supply can only eventuate through the availability of and access to adequate water resources. The largest global consumer of water is agriculture and therefore water availability holds significant importance for food production. Water is also essential to ensure energy security as the extraction and processing of fossil fuels; growing biofuels; and electricity generation, all have high water consumption [8]. At the same time, providing a safe drinking water supply is dependent on energy which is needed for water collection, treatment, and distribution, as well as for wastewater management. Furthermore, energy is required for food production and accounts for approximately 30% of global energy consumption as a result of improved productivity and widespread population growth [9].

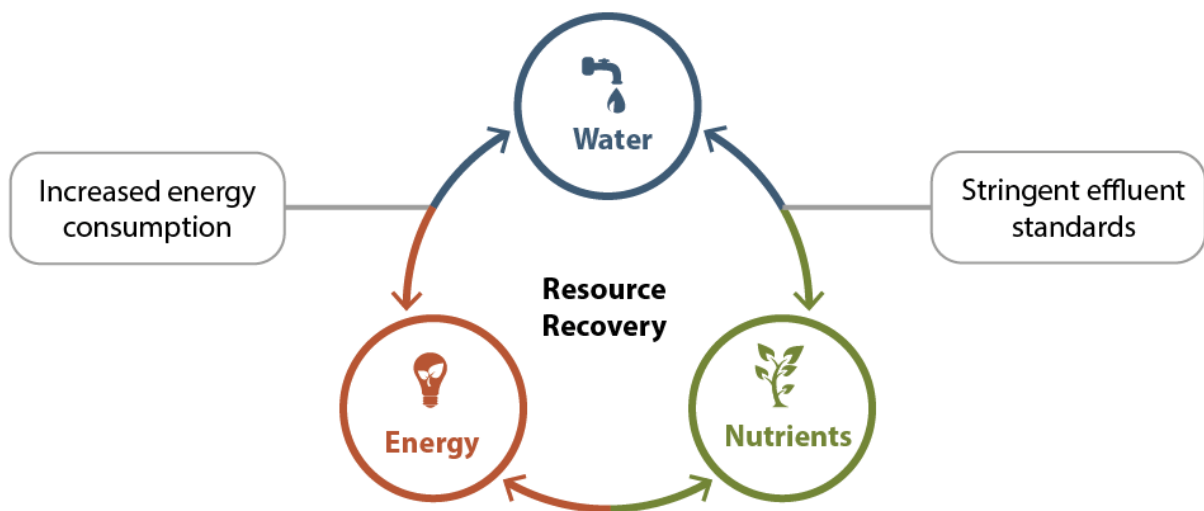


Figure 1.1. The water – energy – nutrient nexus for resource recovery from wastewater.

The nexus between water, energy, and food has always been clearly recognised, yet these resources are traditionally managed independently. Over the coming decades, continued population growth will result in increased international competition and access pressures for existing finite natural resources. Water scarcity is still prevalent in many countries, as 9% of the global population did not have access to improved drinking water sources in 2015 [10]. To add to this, global water demand may increase by as much as 55% by 2050 to meet the requirements of a growing population [9]. A similar situation exists for energy whereby demand could grow by one third by 2035, with 70% growth in electricity demand [9]. Food scarcity can relate to water, land, and fertilizer availability. Fertilizers are essential for agricultural efficiency and to provide for increasing food demand. Worldwide fertilizer production is required to increase between 50 – 100% by 2050 [11]. Specifically, phosphorus is recognised as a dwindling and geographically sensitive natural resource and consequently a secure supply will become vital in the near future.

The expected limitations of natural resources demonstrate the need for an integrated approach and rationalises opportunities to improve their security today. Such an approach effectively considers the interdependence of each sector and aims to develop solutions that align with sustainable development. A range of opportunities exist to improve the security of water, energy, and food. Important to this thesis is the use of waste as a resource in multi-use systems [8]. Wastes, residues, and by-products can be utilised as resources for other products or services and can essentially increase resource efficiency. As an example, the provision of

sanitation facilities to collect and manage wastewater, combined with water reuse practices, reduces freshwater consumption and avoids the spread of disease and environmental contamination [7].

1.1.2. Wastewater treatment to resource recovery

1.1.2.1. Evolution of wastewater treatment

The management of municipal wastewater has undergone considerable development to evolve into a safe and reliable practice. Throughout the 19th century, adoption of sewer systems was aimed primarily to transport untreated wastewater away from cities for environmental disposal. This occurred in response to public health issues whereby the disposal of wastewater into local waterways severely contaminated drinking water sources. Early forms of municipal wastewater treatment began to appear in the 20th century, as cities expanded and environmental pollution became evident [12]. Today, sophisticated systems collect, transport, and treat wastewater to levels of quality set by government legislation to protect the environment as well as encourage water reuse practices. Unfortunately, only 68% of the world's population had access to these improved sanitation facilities in 2015 [10], which emphasises the continued threats to human and environmental health as a result of untreated or inadequately treated wastewater. Although, it is anticipated that by 2030, universal access to basic drinking water, sanitation, and hygiene for households, schools, and health facilities be achieved [13].

Today, the most common wastewater treatment technology is conventional activated sludge (CAS) due to its ability to manage large and highly variable volumes of dilute wastewater with a low hydraulic retention time. The CAS process can also be modified for targeted biological nutrient removal, to meet stringent effluent quality guidelines. Despite its establishment, CAS is recognised as dissipative treatment as organic compounds are either metabolised by suspended bacteria or converted to CO₂ through aerobic processes, which is very energy intensive [14]. As a result, WWTPs have unintentionally emerged as a major energy consumer particularly when effluent standards are high or further tertiary treatment is required for water reuse. The embodied chemical energy of wastewater promotes practices to recover and use this energy to offset the requirements of wastewater treatment. Similarly, nutrient recovery has received growing attention as nitrogen and phosphorus often form the focus of effluent standards and therefore efforts to remove these nutrients may be better utilised by recovering them.

1.1.2.2. Towards resource recovery

Current treatment processes do not effectively recover the resources present in wastewater. In recent years, referred to in the literature as ‘zero-liquid discharge’ [15] and ‘integrated resource recovery’ [7], there has been a paradigm shift from a removal mentality to a recovery standpoint. The most significant benefit would be the ability of WWTPs to supply their own (renewable) source of energy, with further incentives for enhanced water treatment through more efficient nutrient management. Wastewater can currently be purified to a high standard and provide an unconventional water source for potable and non-potable purposes, however energy and nutrient recovery practices are less well established.

Economic feasibility remains the central aspect which has restricted the widespread adoption of energy and nutrient recovery practices. As shown in Figure 1.2, wastewater typically contains less than 0.5% solids, which comprises of energy (organic carbon), ammonia and phosphorus. Given these extremely low concentrations, the work required to recover these components in such a dilute form is simply not viable. Therefore, wastewater treatment has traditionally focused on the removal or suppression of these components from wastewater to meet effluent quality guidelines or to enable water recovery for reuse. Furthermore, a recent investigation into the economic value of wastewater resources has revealed that the value of non-water constituents is estimated to be only 12% of the total value, when assuming total recovery [16]. For these reasons, a trade-off exists for investors as economic benefits may not be directly realised for a number of years, and also because capital and operational costs are currently not well defined [16, 17].

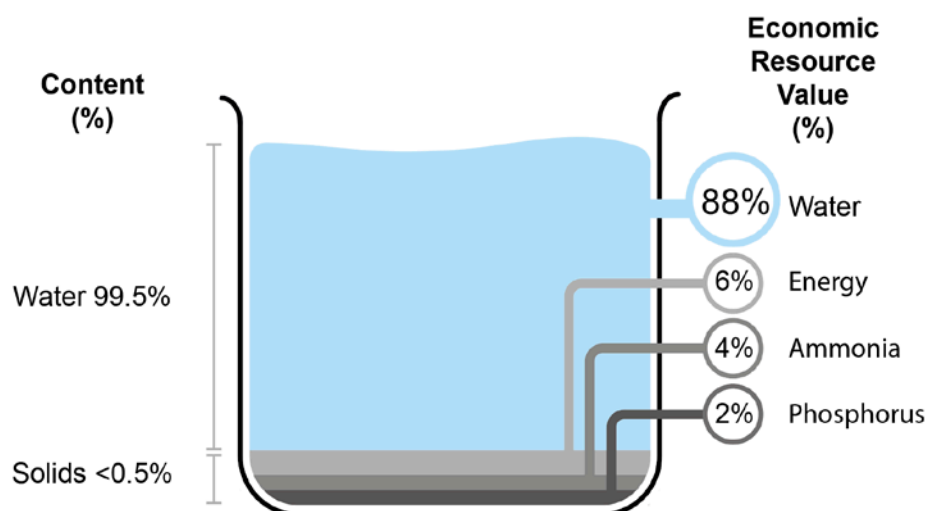


Figure 1.2. Resource content and relative economic value of municipal wastewater [18].

The preservation of freshwater and a reduction in non-renewable resource consumption would represent immediate human and environmental outcomes. Movement towards resource recovery may occur as a result of these drivers, which can have a significant influence on wastewater management decisions. In the case of water recovery from wastewater, treatment costs are considerably higher than conventional water sources. However, without such practices the pollution costs have a far greater consequence and have successfully driven water recovery to become an essential function of modern WWTPs. The same situation could be expected for energy and nutrient recovery, due to the increasing stringency of effluent regulations and the associated increases in energy consumption, alongside demands for renewable energy and alternative phosphorus sources.

1.2. Integrated resource recovery

1.2.1. Water recovery

Water recovery epitomises the key motivation of wastewater treatment, to remove or reduce contaminants to a level safe for humans or the environment. This established practice can be attributed to the alignment with the conventional treatment rationale, in addition to treated water being highly valued both economically and environmentally. The feasibility of the practice also extends to the consideration of regulatory forces to reduce environmental discharge volumes and increase water quality. Other sectors have also contributed to these benefits by accepting reuse water for municipal, agricultural, and industrial purposes [19].

Membrane filtration is an advanced method for water purification with pressure driven membranes being commonplace in modern WWTPs. Membrane bioreactors (MBRs) have also developed as an efficient improvement to CAS systems. However, when established infrastructure is in place and higher qualities are desired, RO membranes are frequently installed. RO is capable of treating water to potable standards, with existing CAS providing convenient pre-treatment. However, most applications are restricted to large-scale WWTPs with well-defined reuse opportunities, due to high capital and on-going costs associated with the pressure input required to drive RO. Although there is potential for innovations to slightly improve the energy efficiency of pressure driven membranes, major developments are unlikely to occur in the near future [6]. Instead, there will be a continued focus on alternative desalination processes that can substitute the electrical energy requirement, with low cost renewable energy sources. Thermally driven processes such as membrane distillation (MD) have gained recent attention as low grade waste heat can be utilised to provide the driving

force and provide excellent effluent quality [20]. In addition, osmotically driven membrane processes such as forward osmosis (FO) are capable of operating with extremely low energy consumption. However, the process alone can only ever provide pre-treatment. For fresh water production, a subsequent desalination process is required to separate the draw solution. Nonetheless, the potential substitution of conventional pre-treatment processes with FO has many advantages.

1.2.2. Energy recovery

Wastewater can have chemical, thermal, and hydraulic energy potential, yet the recovery of chemical energy through anaerobic digestion is the simplest and preferred approach. The chemical energy potential of wastewater is claimed to be between 2 – 10 times the energy required for adequate treatment [21]. These statements rely significantly on the definition of ‘adequate treatment’ as advanced processes require higher energy input to that of conventional methods (Figure 1.3). McCarty et al. [22] estimated that if wastewater typically contains 500 mg COD/L, 100% conversion of all forms of carbon has the potential to produce 1.93 kWh/m³, exceeding the energy requirements of CAS and aerated MBR. When considering advanced treatment such as RO, the chemical energy in wastewater may not be theoretically sufficient to completely cover energy requirements. Nevertheless, this still highlights the potential of the energy source, as well as the pivotal role that high performance low-energy treatment processes can play in achieving energy neutrality.

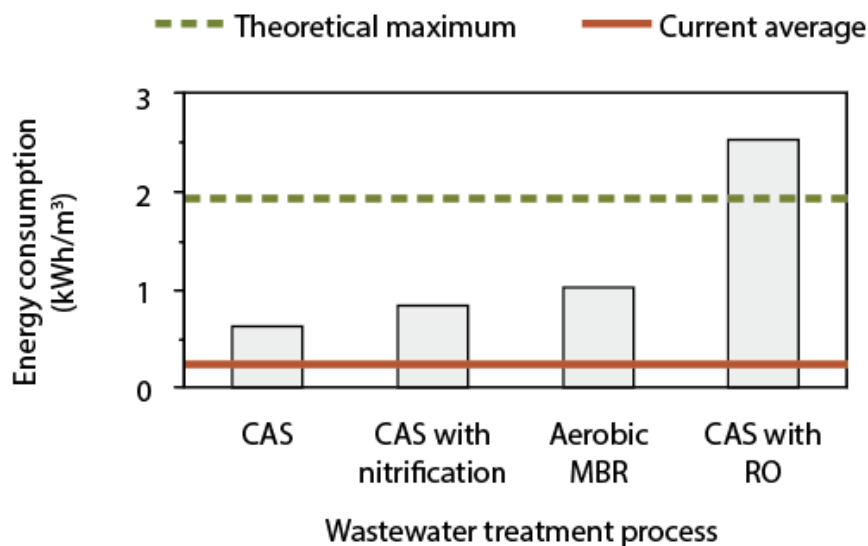


Figure 1.3. Current and achievable targets for chemical energy generation to meet the requirements of wastewater treatment processes, including; conventional activated sludge (CAS), membrane bioreactor (MBR), and reverse osmosis (RO) [23].

Anaerobic digestion is the preferred technology for chemical energy recovery from municipal wastewater, yet the primary reason for adoption of the process is generally for effective sludge treatment. Sludge management at WWTPs can account for up to 50% of total operating costs and therefore a reduction in volume and stabilisation of the by-product is desired [24]. Anaerobic digestion is advantageous as the process can address these requirements with the added benefit of producing methane rich biogas that can be utilised as a renewable energy source. However, sludge digestion can only partially recover the energy potential of wastewater. Firstly, wastewater is very dilute and the CAS process employed to produce sludge suitable for anaerobic digestion is both energy intensive and some chemical energy is oxidised during the process or is inadequately separated [14]. Secondly, the anaerobic digestion process itself is extremely sensitive and requires optimal process conditions to avoid inefficiencies [24]. Lastly, difficulties exist for the efficient capture and conversion of the produced methane [25].

The anaerobic digestion of sludge can be referred to as indirect anaerobic digestion, as raw wastewater has undergone previous treatment to produce a high solids content sludge. An alternative approach involves direct anaerobic digestion, which has been investigated with the aim of replacing aerobic wastewater treatment processes [14, 22, 26, 27]. Despite the advantages of negating aeration requirements a number of impracticalities exist for this approach. As previously mentioned, the high volumes of dilute wastewater would require significant heating requirements to attain optimal conditions, in combination with comparatively low COD removal and the difficulties associated with subsequent management of nutrients which remain in the liquid effluent. Complications of methane recovery would be further aggravated as the effluent volume is larger. Therefore, direct anaerobic digestion is unlikely to be a feasible approach to energy recovery and methods that maximise the energy generation potential of indirect anaerobic digestion systems should become a focus. Furthermore, developments in anaerobic membrane bioreactors (An-MBR) present a significant improvement over conventional reactor layouts [28].

1.2.3. Nutrient recovery

Nutrient recovery from wastewater has received growing attention in recent years as a result of increasingly stringent effluent standards, as well as concerns for phosphorus security. Although nutrients exist in very small concentrations within wastewater, nitrogen and phosphorus content are often the focus of effluent regulations. When effluent is intended for environmental release in sensitive receiving waters, excessive nutrient loadings can cause

eutrophication. Similarly, removal of these compounds is required when water reuse is intended. Methods are well established to reduce nutrient levels to regulatory levels; however recovery of nutrients from such a dilute and complex matrix is significantly more complicated.

Methods to recover nitrogen as ammonium include ion exchange, struvite precipitation and stripping [15]. However, for these methods to be economically feasible the concentrations are generally required to exceed 5 g $\text{NH}_4\text{-N/L}$. Wastewater typically contains less than 0.1 g $\text{NH}_4\text{-N/L}$ [29] and therefore it is more practical to remove nitrogen from wastewater using nitrification/denitrification processes. Similar recovery methods are available for phosphorus, however the same limitations are present and relate to the low phosphate concentrations in wastewater of approximately 8 mg/L [22]. A common removal method involves precipitation by salt addition, but results in the phosphate being in a less chemically available form to enable recovery. On the other hand, phosphorus can also be biologically accumulated and has a higher recovery potential, particularly when anaerobically digested. In both situations, the challenge remains to first produce a concentrated stream of nutrients, and then to apply the previously mentioned recovery techniques.

One promising opportunity for nutrient recovery at WWTPs involves the liquid effluent produced from anaerobically digested sludge. The anaerobic digestion of concentrated wastewater and subsequent dewatering produces a nutrient-rich liquid, also termed digested sludge centrate. Despite the high concentrations of nutrients, they are still insufficient to provide economically viable recovery. Further concentration of this stream is required and can be achieved by implementing pre-concentration processes to concentrate nutrient levels whilst simultaneously extracting clean water [30]. Nutrient recovery from digested sludge centrate may be a feasible side-stream process that can be integrated easily with current wastewater infrastructure. Although both nitrogen and phosphorus may be recovered in an integrated manner, a greater focus is required to develop phosphorus recovery due to global drivers. Experts predict that phosphorus recovery from wastewater will be practiced over the next 20 years in industrialized countries for economic reasons [31]. However, this significantly depends on the market price for mined phosphorus and the efficiency of the implemented recovery processes.

1.3. Strategies to maximise the recovery of resources

Strategies to maximise the recovery of resources from municipal wastewater focus on avoiding or handling such a dilute and complex mixture [14, 15, 32]. Energy and nutrient recovery is simply not economically viable when using current technologies and practices. Intervention at both the household and WWTP level may be required, with source separation, co-digestion, and pre-concentration representing three feasible strategies to facilitate maximum resource recovery.

1.3.1. Source separation

Source separation is a notable strategy to maximise resource recovery as the problem of dilution is essentially avoided. Wastewater can be divided into concentrated black water and less concentrated grey water. The concentrated streams could effectively undergo direct anaerobic treatment for energy recovery, and dilute streams would present a more favourable approach to water recovery. Furthermore, urine can be source separated from black water for nutrient recovery, as urine contains high concentrations of nitrogen and phosphorus. Separating wastewater at the source presents more tangible resource recovery opportunities, however the considerable infrastructural investment associated with upgrading collection systems has often limited its implementation [33].

1.3.2. Co-digestion

An alternative strategy to address the dilute nature of municipal wastewater is to encourage the disposal of other organic wastes to maximise energy recovery through co-digestion at WWTPs. This can be achieved by encouraging households to add kitchen waste to wastewater using grinders. Otherwise, on a community scale waste could be disposed of directly to digesters at WWTPs, including organics originating from municipal solids waste, industrial by-products or agricultural crop residues. The latter is more favourable, as addition at households may not significantly increase wastewater concentrations and would still require separation processes at the WWTP prior to anaerobic digestion. At the same time, co-digestion at the WWTP does not directly resolve the issue of dilute wastewater and therefore pre-concentration techniques in combination with co-digestion would be desirable.

1.3.3. Pre-concentration

Pre-concentration is the term that denotes an advanced concentration process to increase the amount of organic matter separated from wastewater so that energy and nutrient recovery

becomes more feasible. Unlike source separation or the addition of other organics, pre-concentration manages dilute wastewater at a centralised WWTP. Pre-concentration would be most effectively implemented if applied to raw wastewater, however additional opportunities do exist. Since pre-concentration essentially describes a separation technique that results in clean water and a concentrated stream, this strategy could in fact be implemented at many stages of WWTPs. Current WWTP processes essentially perform pre-concentration, however an increased emphasis on maximising recovery is required and a major limitation involves the need for further treatment to recover high quality water. This results in the heightened need to reinvent and optimise wastewater treatment for integrated resource recovery. This idealistic objective personifies efforts to purify wastewater and with continued technological development, may be realised for new or re-developments in the near future.

1.4. Pre-concentration opportunities at wastewater treatment plants

Pre-concentration could be effectively applied at a number of stages during wastewater treatment, with Figure 1.4 presenting a possible scenario. Firstly, primary treatment aims to remove suspended solids and can be achieved by gravity separation in clarifiers as well as fine screening. The pre-concentration process would then recover high quality water whilst simultaneously concentrating organic compounds. The resultant sludge from both primary treatment and pre-concentration would then undergo anaerobic digestion to produce biogas for energy production, utilising a combined heat and power (CHP) system. Solids and liquid from the digester are separated to produce biosolids and sludge centrate respectively. Biosolids are utilised for beneficial reuse, whilst centrate can undergo further processing to concentrate nutrients to enable phosphorus recovery. The composition of the remaining liquid is highly dependent on the rejection of each pre-concentration technique. Ideally, this stream would have a very low volume and the additional process that would be required for the concentrate management may involve a low energy nitrogen removal technique.

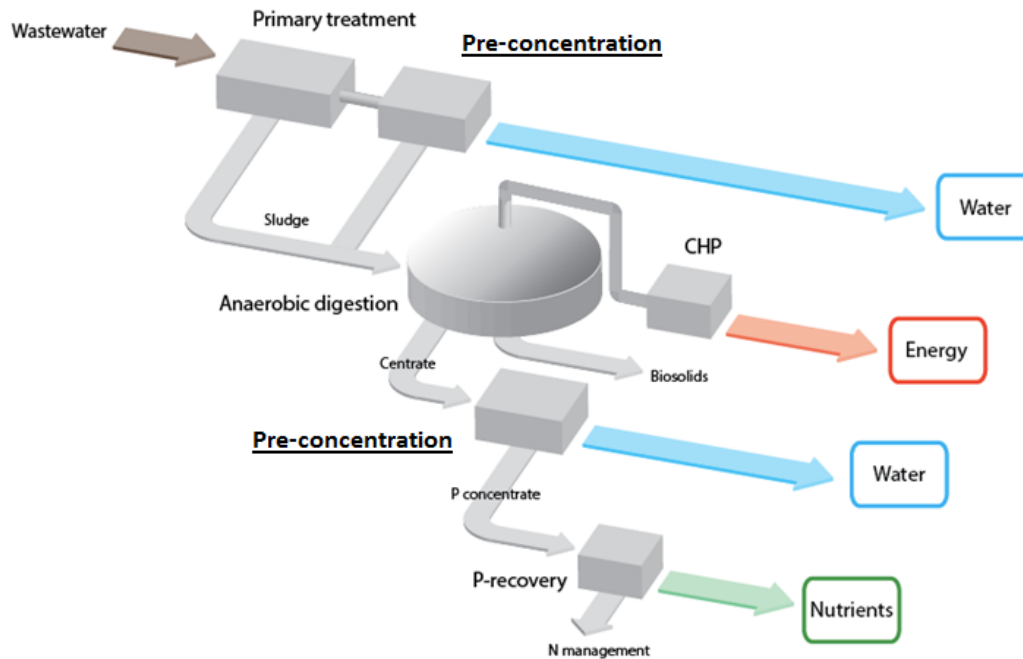


Figure 1.4. Pre-concentration based flow sheet for integrated resource recovery. Pre-concentration processes enable water and nutrient recovery, whilst energy is produced from anaerobic digestion, utilising a combined heat and power (CHP) system.

1.5. Objectives and thesis scope

The aim of this thesis is to evaluate the feasibility of applying FO for resource recovery from wastewater. The specific objectives are to:

1. Develop a draw solute selection protocol for processes that integrate FO with anaerobic treatment, namely to understand the effects of reverse solute flux on anaerobic treatment;
2. Clarify the effects of draw solution selection and operational conditions associated with FO pre-concentration of wastewater, in terms of water flux performance, salinity build-up, and membrane fouling;
3. Elucidate FO membrane fouling and the efficiency of physical membrane cleaning during the filtration of high suspended solution solutions (i.e. raw wastewater and digested sludge centrate) in resource recovery applications;
4. Determine suitable operating conditions when integrating FO with anaerobic treatment, through optimising membrane selection, water recovery, and concentrate digestibility.

5. Demonstrate phosphorus recovery from digested sludge centrate using a seawater-driven FO system and investigate the viability of the process.

1.6. Thesis outline

This thesis contains eight chapters and comprises two major research components (Figure 1.5). Chapter 2 provides a critical assessment of the literature currently available on FO and its application to resource recovery. The first major research component focuses on evaluating the effects of operating conditions on FO performance (i.e. Chapters 3 – 5). Chapter 3 develops a protocol for FO draw solution selection pertaining to applications that integrate FO with anaerobic treatment. In Chapter 4, various factors (i.e. operating conditions) are assessed and their individual and combined effects on FO performance and resource recovery potential are evaluated. Chapter 5 systematically investigates physical membrane cleaning techniques that are necessary for optimising the FO process in this context. The second component of this thesis presents two key demonstrations of FO applications for resource recovery, each utilising the optimised parameters presented in Chapters 3 – 5. Firstly, Chapter 6 elucidates the process performances and challenges of integrating FO with anaerobic treatment for simultaneous wastewater treatment and resource recovery. Secondly, Chapter 7 presents a novel approach to phosphorus recovery that exploits some key advantages of the FO process. The conclusions and recommendations of this thesis are lastly presented in Chapter 8.

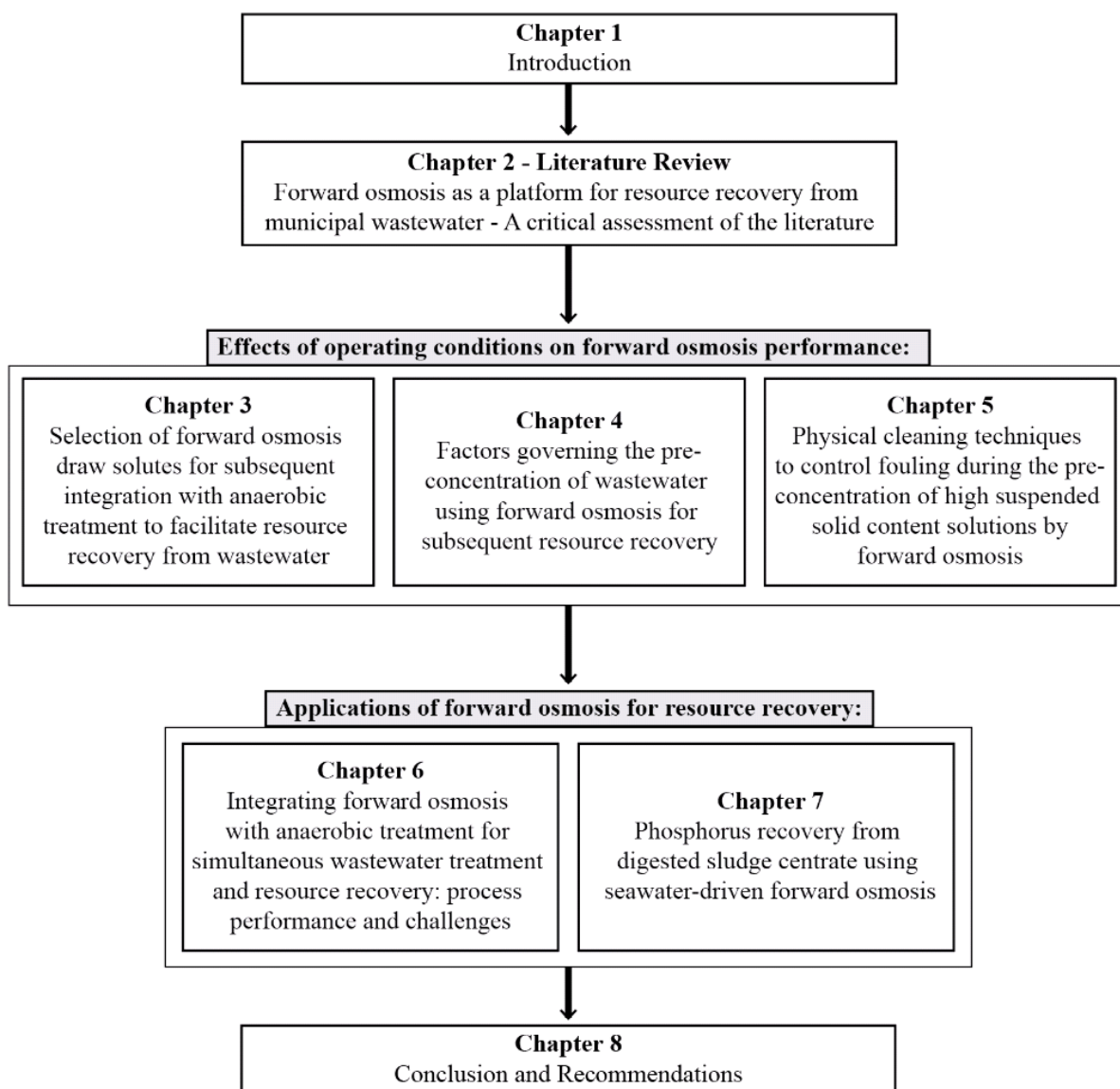


Figure 1.5. Thesis outline.

CHAPTER 2: Forward osmosis as a platform for resource recovery from municipal wastewater – A critical assessment of the literature

Corresponding publication:

A.J. Ansari, F.I. Hai, W.E. Price, J.E. Drewes and L.D. Nghiem, Forward osmosis as a platform for resource recovery from municipal wastewater - A critical assessment of the literature, Journal of Membrane Science, 529 (2017), 195-206.

2.1. Introduction

The recovery of water, energy, and nutrient resources from municipal wastewater presents a promising solution to a number of prevalent economic, environmental, and social issues. Wastewater reclamation can address both water scarcity and environmental pollution [6, 34]. Utilisation of the biogas produced from the organic content of wastewater can offset the energy requirement for treatment [35]. Nutrient recovery from wastewater also deserves special attention due to the increasing stringency of effluent discharge regulations and uncertainties associated with minable phosphorus supply for food security [36-38]. Increasing awareness of the potential resource value of municipal wastewater has prompted significant research efforts to synergise emerging wastewater treatment processes and resource recovery techniques [7, 35, 39].

Activated sludge treatment is an established biological process that focuses primarily on purifying wastewater of organic matter, pathogens, and nutrients, but does not effectively facilitate energy and nutrient recovery. Activated sludge treatment is energy intensive due to the high electricity demand for aeration and also produces excessive amounts of sludge residuals [40]. During activated sludge treatment, the carbon (i.e. chemical energy) and nitrogen (i.e. nutrient) contents of wastewater are converted to biomass, carbon dioxide, and nitrogen gas. In other words, much of the energy and nutrient contents of wastewater are dissipated at the expense of significant energy input. As an alternative, anaerobic treatment converts organic substances into methane rich biogas in the absence of oxygen and transforms phosphorus to a more chemically available state for subsequent recovery [28]. Transitioning from aerobic towards anaerobic based treatment processes has significant potential to lower the energy consumption of wastewater operations (i.e. by avoiding

aeration), as well as achieve energy-neutral wastewater treatment (i.e. through biogas production) [14, 22, 41-45].

The opportunity for wastewater treatment plants (WWTPs) to provide a renewable source of useful heat and electricity through biogas conversion is immense [46, 47]. In fact, the chemical energy content in municipal wastewater exceeds the electricity requirement of operating an activated sludge plant by at least nine times [48]. Despite this significant embedded energy content, there are a number of major challenges that currently restrict the feasibility of directly anaerobically digesting raw wastewater for energy recovery. The concentration of organic matter in wastewater is typically low. Therefore, a sufficient organic loading rate cannot be maintained in the anaerobic digester, resulting in a low biogas yield and inadequate removal of organic pollutants from wastewater. In addition, since methane is slightly soluble in water (22.7 mg/L), at a low biogas yield much of the generated methane can be lost via effluent discharge [28]. Several membrane filtration technologies have been integrated with anaerobic treatment to overcome these challenges, aiming to improve the retention of biomass in the reactor and to increase effluent quality. Anaerobic membrane bioreactors (An-MBRs) utilising low pressure membranes such as microfiltration (MF) or ultrafiltration (UF) is a notable approach. Nevertheless, the MF/UF membranes used in conventional An-MBRs cannot retain dissolved organic carbon. Thus, they are not effective for energy recovery and cannot produce a high effluent quality [28].

Further developments in An-MBR technology have resulted in the novel hybridisation of MBR with high retention membrane processes including nanofiltration (NF), reverse osmosis (RO), membrane distillation (MD), and forward osmosis (FO) [49]. Among these high retention membrane processes, FO stands out as the most promising candidate for integration with anaerobic treatment due to a combination of high separation efficiency and high fouling reversibility [50-53]. The integration of FO with anaerobic treatment has been widely reported in the literature [54-58]. FO is a unique membrane process that utilises the physical phenomenon of osmosis to transport water across a semipermeable membrane. As a major advantage, the FO process can operate with minimal external energy input [59]. However, further treatment of the draw solution is required to extract fresh water and can be achieved using pressure or thermally driven membrane processes [60]. Lutchmiah, et al. [61] provided a critical assessment of FO applications for water reclamation. They also highlighted the need to develop new membrane materials and optimise draw solute selection as well as key operating conditions to facilitate full-scale implementation of FO for water reclamation

applications [61]. In another excellent review, Holloway, et al. [62] systematically summarised and reviewed all relevant works related to osmotic membrane bioreactors for the production of high quality potable water from impaired sources including wastewater. A report by Xie, et al. [39] in particular identified the untapped potential of FO amongst several other membrane separation processes for recovering nutrients from municipal wastewater. Indeed, there is growing support that FO has the potential to be an important technology in the future of wastewater treatment [59, 61, 63, 64].

Integrating FO with anaerobic treatment is essential for energy and nutrient recovery. The viability of the anaerobic osmotic membrane bioreactor (An-OMBR) has been demonstrated where the FO membrane is submerged inside the anaerobic bioreactor [54, 56, 57]. An alternative approach uses FO to firstly pre-concentrate raw wastewater to a high strength for subsequent anaerobic treatment. The concept of wastewater pre-concentration is yet to be fully explored, but it holds significant opportunities for resource recovery applications. Preliminary investigations into process efficiency [65, 66] have been conducted. However, issues of draw solution selection, salinity accumulation, membrane fouling, and anaerobic treatment integration have not been adequately addressed.

This chapter critically reviews recent applications of FO for recovering energy and nutrients from municipal wastewater by integrating with existing resource recovery techniques (i.e., anaerobic digestion and phosphorus precipitation) and other complementary processes (e.g., MD and RO) for clean water extraction. The challenges and potential opportunities associated with FO-based treatment processes are evaluated in terms of treatment efficiency and resource recovery potential. The outlook of an integrated FO membrane-based system for simultaneous wastewater treatment and resource recovery is discussed. A research roadmap for further development of FO for resource recovery from wastewater is also outlined and discussed.

2.2. Forward osmosis

Water transport during FO is driven by an osmotic pressure difference across a semipermeable membrane. The water flux (J_w) can be expressed in terms of the water permeability coefficient of the membrane (A) and the bulk osmotic pressure of the draw solution ($\pi_{D,b}$) and the feed solution ($\pi_{F,b}$):

$$J_w = A(\pi_{D,b} - \pi_{F,b}) \quad \text{Equation 2.1}$$

This expression however, relies on the assumption that an ideal membrane is used whereby the draw solute does not diffuse back into the feed solution, as well as the existence of a perfect concentration (osmotic pressure) gradient between both sides of the membrane. The latter relates to the complex associations between concentration polarization; reverse solute flux; and membrane fouling, which exist as a result of feed and draw solution chemistry; membrane characteristics; and operating conditions [67]. Each of these factors contribute to the lower than expected flux behaviour observed during FO operation, which remains the most significant challenge for the viability of the FO process.

2.2.1. Forward osmosis membranes

FO membranes have an asymmetric structure and are composed of an active and support layer. The active layer has a dense selective structure and the support layer is porous to provide mechanical support. Until recently, the most widely available FO membrane is a cellulose triacetate (CTA) membrane by Hydration Technologies Innovation (HTI). CTA membranes are reported to be chlorine resistant and are reasonably robust in terms of thermal, chemical, and biological degradation [61]. Unfortunately, these properties limit the flux performance of the membrane as the thickness of the support layer reduces the osmotic driving force as a result of internal concentration polarisation (ICP). Newly developed, thin-film composite (TFC) membranes reduce the extent of ICP and consist of a selective polyamide active layer, with a polysulfonate support layer [68]. The TFC membrane also provides increased permeability and a wider pH tolerance, but mechanical stability still requires further improvement [61]. Cross-sectional SEM images of each membrane are shown in Figure 2.1 and demonstrate the remarkably different structural characteristics. It is noteworthy to mention that the CTA FO membrane produced by HTI is no longer commercially available. Instead, Porifera Inc. has emerged as the market leader in FO membrane manufacture and provides only TFC membranes.

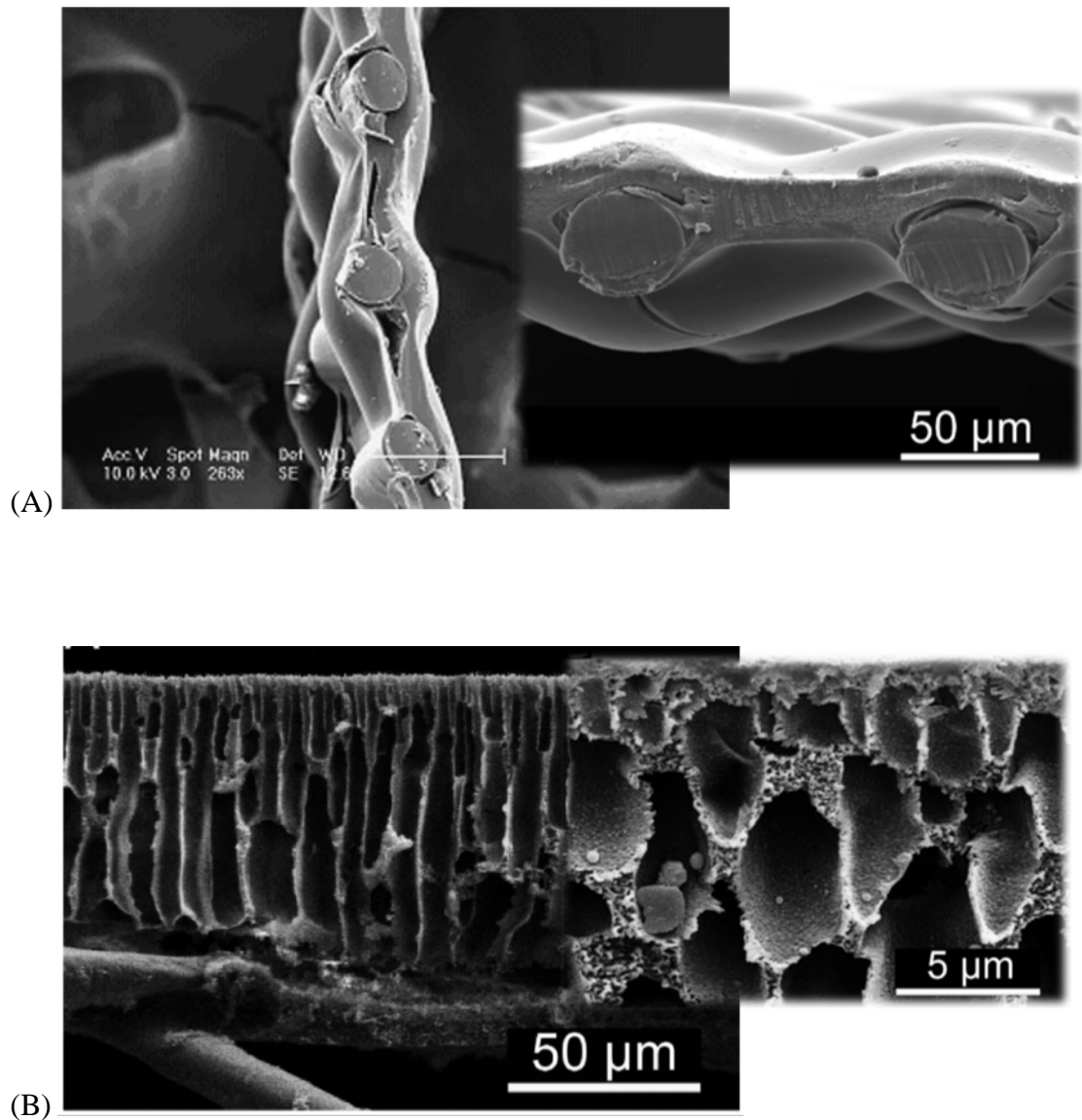


Figure 2.1. Cross-sectional SEM images of (A) CTA FO membrane – polyester mesh embedded within the polymer material and (B) TFC FO membrane – polyamide with PET non-woven fabric support. Figure adapted from Cath, et al. [69] and Yip, et al. [70].

Because FO membranes have an asymmetric structure, two options for membrane orientation exist. FO mode refers to when the active layer faces the feed solution and pressure retarded osmosis (PRO) mode is when the active layer faces the draw solution. The selected orientation has a significant effect on FO performance in terms of flux behaviour and membrane fouling. Larger permeate water flux can be observed when operated in PRO mode as the draw solution is in contact with the active layer and therefore is not affected as severely by ICP. On the other hand, in PRO mode membrane fouling is more prominent as the support layer is in contact with the feed solution [61]. As a result, it is widely accepted that for wastewater applications FO mode provides the most fouling resistant orientation, due

to the active layers high rejection characteristics and lower flux environment. For these reasons, the FO mode (i.e. active layer facing the feed solution) is exclusively applied throughout this thesis.

2.2.2. Configurations

FO membrane configurations can include spiral wound, hollow fibre, and plate and frame. The ideal configuration is the one which can provide the highest membrane packing density, however additional consideration must be given to the way in which the feed and draw solutions contact the membrane. Spiral wound FO membranes provide a high packing density, but high fouling wastewater can increase concentration polarisation and potentially clog spacers. Hollow fibre membranes are self-supported and can also be arranged with a high packing density. The plate and frame configuration is known to be most suited to wastewater applications, since high cross-flow velocities can be attained (reducing concentration polarisation) as well as allowing sufficient backwashing or cleaning to take place [61]. Because of this arrangement however, plate and frame configurations are more expensive than others.

2.2.3. Draw solutes

The draw solution provides the osmotic driving force for the FO process and is therefore a significant factor in determining FO performance. A range of criteria for the selection of suitable draw solutions has been developed [71, 72], namely the pre-requisite parameter is that the draw solution must have a higher osmotic pressure than the feed solution. Solutes that can generate high osmotic pressures are often highly soluble and have a low molecular weight [73]. Furthermore, other desirable factors that make suitable draw solutions include low reverse solute flux, high diffusion coefficient, low viscosity, and membrane compatibility [73, 74]. The cost of the draw solution should also be taken into account as replenishment costs could significantly enhance the operating costs of FO. An additional consideration is the recovery or use of the diluted draw solution, as these processes essentially determine the energy efficiency of the system [71]. Alongside the developments required for membrane materials, research into the application or development of novel draw solutions remains an integral component for the future of FO, particularly in a wastewater treatment context. When considering the limitations of membrane materials, although desirable, a perfectly semipermeable membrane may not be possible and therefore these constraints may rely on developments in other areas.

2.2.4. Concentration polarisation

Concentration polarization is an inherent limitation for high retention membrane processes, but FO is further complicated by the presence of the draw solution. Figure 2.2 illustrates the concentration profile for an asymmetric membrane operated in FO mode, whereby the effective osmotic driving force ($\Delta\pi_{eff}$) across the membranes active layer is substantially lower than the bulk osmotic pressure difference ($\Delta\pi_b$) between the feed and draw solutions. As shown, external concentration polarization (ECP) can occur on both the feed and draw side of the membrane, and describes the concentration or dilution of the bulk solution close to the membrane surface boundaries. Though, ECP has shown to have a minimal effect on flux decline in FO when the cross-flow velocity is increased [75].

By contrast, internal concentration polarisation (ICP) occurs within the porous support layer of the membrane and has a significant effect on FO performance as mitigation methods are limited. ICP is unique to FO as unlike RO, the support layer is in direct contact with the draw solution and plays an active role in providing the driving force for water transport. During FO mode, dilutive ICP occurs due to the difference in concentrations on the boundaries of the support layer and results in a significant reduction in water flux. The performance limiting effects of ICP have been found to be far greater than that of ECP and therefore reducing the effects of ICP remains a focal point for development of FO membranes and draw solution optimisation [76].

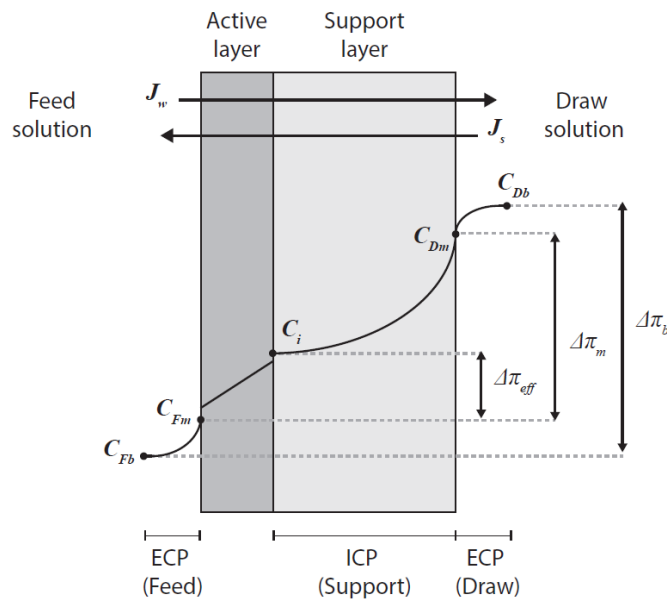


Figure 2.2. Concentration profile for asymmetric FO membrane (FO mode) demonstrating external concentration polarisation (ECP) of the feed and draw solutions; and internal concentration polarisation (ICP) within the support layer.

2.2.5. Reverse solute flux

Reverse solute flux describes the diffusion of solutes from the draw solution through the membrane and into the feed solution, opposite to the direction of water flux. This occurs because the membrane is not ideally impermeable to all solutes and the large concentration difference permits diffusion. Reverse solute flux can be affected by the membrane structural characteristics, as well as by the physiochemical properties of the draw solution [77]. Reverse solute flux is recognised as a significant impairment of the FO process due to a number of reasons. Migration of the draw solute across the active layer can lead to concentration polarisation, particularly within the fouling layer on the feed side of the membrane and reduces the effective osmotic pressure [51, 78]. Additionally, replenishment of the lost draw solute is required and would increase operating costs. Reverse solute flux also restricts a number of FO applications, when contamination of the feed solution by the draw solute is undesirable. These include food concentration and drug release applications [79], however limitations may also exist for wastewater treatment and desalination applications, particularly in relation to FO concentrate management or disposal [61].

2.2.6. Membrane fouling

FO is widely recognised as having a lower fouling propensity compared to pressure driven membranes due to the difference in driving force [51]. During RO the large hydraulic pressure required to generate high water flux creates a highly compacted fouling layer that cannot be easily removed by hydraulic means. Whereas during FO, even at an identical permeate flux the nature of the osmotic driving force creates a less dense fouling layer and therefore the flux can be completely recovered in some scenarios. Therefore, the lower fouling propensity experienced during FO relates to the reduced occurrence of irreversible fouling. Nevertheless, membrane fouling is still an issue for FO and further research is required to better understand fouling mechanisms, as well as to develop strategies to reduce the effects of membrane fouling.

The complexities of membrane fouling have led to a number of studies attempting to understand the fouling mechanisms which occur during FO. Studies on organic fouling [80-85], inorganic fouling [86-88], and biofouling [89-91] have emerged with a focus on wastewater as the feed solution. A number of factors affect FO membrane fouling, with flux decline behaviours reported to be distinctly different depending on the foulant type and characteristics, employed draw solution, and other process parameters [51]. There is

however, a lack of long-term operational demonstrations of direct FO treatment of wastewater that focus on membrane fouling.

One important fouling mechanism which can lead to severe FO flux decline is cake-enhanced osmotic pressure (CEOP). CEOP occurs due to solute trapping between the fouling cake layer and the active layer of the membrane, as a result of reverse solute flux [51]. This causes the osmotic pressure on the feed side to dramatically increase, leading to an associated drop in the effective osmotic pressure difference and therefore driving force across the membrane. It is important to note that the flux decline is not attributed to the cake layer resistance, but because of concentration polarisation. The solute transport properties of the draw solutions are therefore extremely important and it has been shown that draw solutes such as sodium chloride which have a large reverse solute flux, can accelerate CEOP, leading to unsustainable FO operation [51].

A number of studies have demonstrated that organic and inorganic fouling can be successfully mitigated by optimising the feed hydrodynamic conditions without employing chemical cleaning [67, 80, 92]. Yet, there is still a significant focus on the most sustainable operational and cleaning protocols to tolerate membrane integrity and to reduce flux decline. Overall, the least invasive techniques of physical hydraulic cleaning have shown excellent results in terms of flux recoverability. Hydraulic cleaning can significantly affect the structure of the organic fouling layer which removes the hydraulic resistance cause by the layer and which is responsible for flux decline.

2.2.7. Draw solute regeneration and water recovery processes

Wastewater treatment by FO is generally recognised as a pre-treatment process when recovery of potable water is desired. The draw solution requires an additional desalination process such as RO, nanofiltration (NF) or MD, to extract clean water, as well as replenish the draw solute concentration in the draw solution (rejected brine recycle) in order to regenerate the osmotic driving force [93]. Despite the disadvantages associated with the energy input required to operate these systems, the constituents of the draw solution can be controlled and therefore so too can the feed water conditions for the regeneration process. Thus, FO can represent a potentially ideal pre-treatment system for subsequent desalination processes. Furthermore, the integration of energy recovery via anaerobic digestion can be justified when considering the energy involved to operate draw solute regeneration systems.

For example, the produced heat from co-generating biogas could be beneficially utilised by the MD process.

The combination of forward osmosis – membrane distillation (FO-MD) has emerged as a potentially viable hybrid system since heating requirements could be provided by renewable sources such as solar, waste heat or biogas powered CHP systems [94]. This being said, there are limited studies which compare the effectiveness of regeneration methods in terms of energy efficiency, particularly in relation to draw solution selection and concentration. Some studies have included analysis within draw solution selection, however these are limited to either RO [72] or NF [95]. Therefore, a comprehensive energy balance is yet to be conducted for FO-MD systems. Furthermore, a limited number of studies specifically focus on the optimisation of FO hybrid systems, with only basic performance parameters [96] and novel applications [97, 98] being emphasised at this stage.

Other opportunities have also been explored as an attempt to avoid the high energy costs of recovering water from the draw solution. This alternative involves utilising a draw solution that can be directly used or discharged into the environment after dilution by the FO process. Firstly, readily available solutions such as seawater or RO brine have gained attention as potential draw solutions [99]. These could provide a significantly lower cost wastewater management strategy in some areas, however the major disadvantage is that the process does not produce clean water for alternative uses. The use of nutrient solutions has been demonstrated, particularly for emergency applications whereby the diluted draw solution can be directly consumed [69]. Additionally, concentrated liquid fertilizers have been considered for use as a draw solution to extract clean water from impaired sources and provide a nutrient source for fertigation purposes [100, 101].

2.3. Forward osmosis for wastewater treatment

Interest in applying FO to wastewater treatment has grown significantly in recent years [60, 61, 63, 79, 99, 102]. These potential applications are motivated by several advantages of FO over current wastewater treatment technologies. Given its good fouling reversibility, FO can be directly applied to a complex solution without extensive pre-treatment [103]. High rejection of dissolved contaminants is another important advantage of FO for wastewater treatment. When FO is combined with a draw solute recovery process, clean water can be produced from the draw solution, furthering water reuse opportunities. These unique features

of FO have spurred the development of several system configurations for wastewater treatment and water reclamation.

2.3.1. Forward osmosis system configurations for wastewater treatment

Three major system configurations have been developed for FO wastewater treatment applications and vary depending on the type of solution in contact with the FO membrane (Figure 2.3). Firstly, the most widely recognised approach is the aerobic osmotic membrane bioreactor (Ae-OMBR) [104-110] whereby wastewater is fed into an activated sludge reactor (Figure 2.3A). Secondly, several research groups have explored the potential of An-OMBRs [54, 56, 57] for wastewater treatment and the production of biogas (Figure 2.3B). Both OMBR configurations typically utilise a submerged FO module, as the high solids content of the mixed liquor and digested sludge can cause blockages in other arrangements. The third configuration (Figure 2.3C) adopts a similar approach to the An-OMBR (Figure 2.3B). However, in this configuration, wastewater is firstly pre-concentrated by the FO membrane prior to anaerobic digestion [65, 66, 111, 112]. A key benefit of this configuration is that the FO membrane is in contact with concentrated wastewater, which has lower fouling propensity compared with the mixed liquor inside an An-OMBR. Similar to conventional MBRs, the submerged configuration appears most suited for wastewater pre-concentration as it avoids the costs associated with circulating the feed solution through an external membrane module [113].

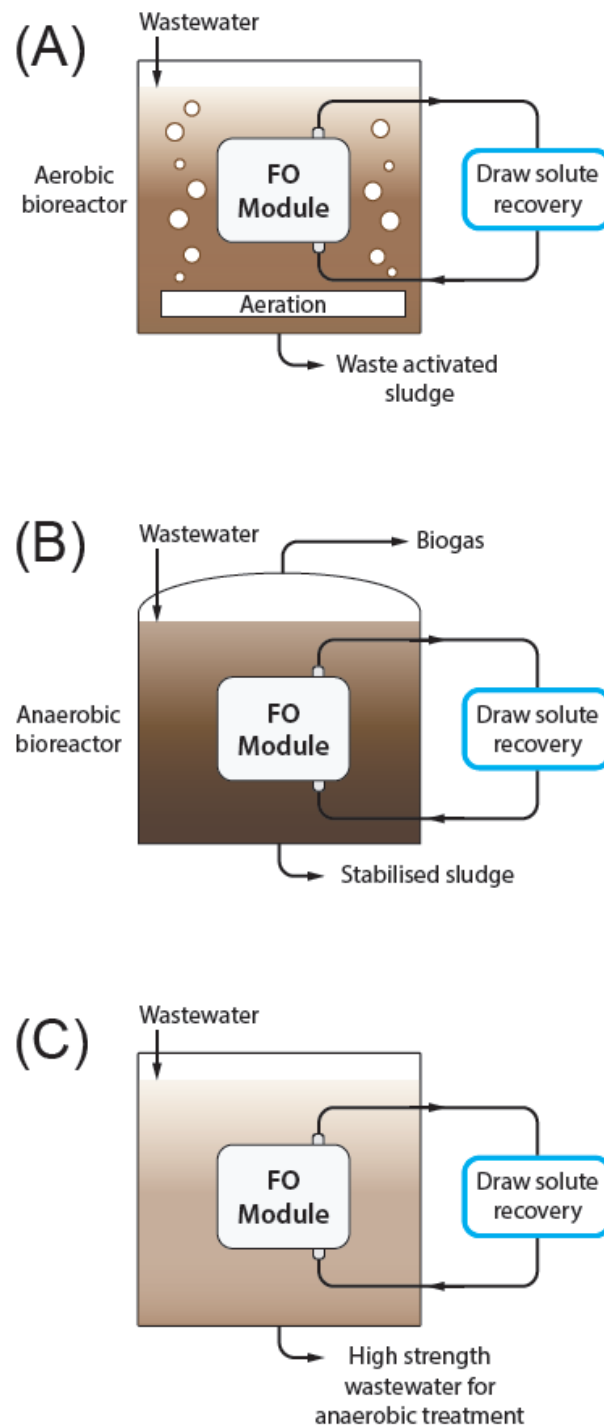


Figure 2.3. Schematic representation of three major FO system configurations for wastewater treatment: (A) Ae-OMBR, (B) An-OMBR, and (C) wastewater pre-concentration intended for subsequent anaerobic digestion.

2.3.2. Treatment performance of forward osmosis systems

The level of treatment provided by each FO system can differ considerably, due to the type of biological treatment applied, process conditions, and membrane properties (Table 2.1). The treatment performance of an FO system is generally indicated by the removal efficiency of organic matter, nitrogen, phosphorus, and trace organic contaminants (TrOCs).

In all the FO system configurations discussed above, a high removal efficiency of a broad range of contaminants can be achieved, since FO membranes are highly effective at retaining organic compounds, colloidal particles, and microbes in the feed solution (Table 2.1). Similarly, FO membranes have consistently demonstrated near complete rejection of phosphorus for two reasons. Electrostatic repulsion occurs between negatively charged phosphate ions and the negative surface charge of the FO membrane, deterring phosphate transport through the membrane. Another important rejection mechanism for phosphorus is size exclusion, as phosphate has a large hydrated radius [114]. The superior rejection capability of FO membranes for organic matter and phosphorus has far reaching implications for wastewater treatment and resource recovery. To highlight this point, conventional An-MBRs (i.e. which utilise MF or UF membranes) cannot achieve sufficient phosphorus removal and have a significantly lower organic matter removal efficiency compared to An-OMBRs [56]. Thus, the integration of FO with anaerobic treatment in the form of An-OMBR can significantly improve the overall system treatment capacity and viability for wastewater treatment.

Table 2.1. Summary of FO wastewater treatment performance in terms of the removal efficiency of organic matter (i.e. total organic carbon (TOC) and chemical oxygen demand (COD)), phosphorus (i.e. total phosphorus (TP)), and nitrogen (i.e. NH_4^+ -N and total nitrogen (TN)).

FO system configuration	Membrane (arrangement)	Removal Efficiency (%)					Ref.
		Organic matter		Phosphorus	Nitrogen		
		TOC	COD	TP	NH ₄ ⁺ -N	TN	
Ae-OMBR	CTA (cross-flow)	98%	-	-	99%	-	[115]
	TFC (cross-flow)	96%	-	-	99%	-	[115]
	CTA (submerged plate-and-frame)	-	>99%	>99%	-	>82%	[106]
	CTA (submerged plate-and-frame)	98%	-	>99% PO ₄ ³⁻	80-90%	-	[108]
	CTA (submerged plate-and-frame)	98%	-	-	98%	-	[116]
	CTA (submerged plate-and-frame)	>98%	-	-	>98%	-	[52]
An-OMBR	CTA (submerged plate-and-frame)	-	>95%	>99%	FO only Ammonia = 70-80%	-	[56]
	CTA (submerged plate-and-frame)	-	96.7%	99%	60%	-	[54]
	CTA (submerged plate-and-frame)	92.9%		-	-	-	[57]
Wastewater pre-concentration	CTA (submerged plate-and-frame)	-	99%	99% PO ₄ ³⁻	Ammonia = 67-68%	56-59%	[117]
	CTA (pilot-scale spiral wound)	-	99.8%	99.7%	48.1%	67.8%	[66]

The removal of nitrogen by FO-based systems is highly variable and depends on the structure of nitrogen bearing compounds in the solution and the biological treatment process [118] (Table 2.1). FO membranes alone have an incomplete rejection of neutral ammonia (i.e. <80%) [56, 117] compared with positively charged ammonium ions [114]. At neutral pH, Ae-OMBRs can provide some nitrogen removal capacity as a result of both biological degradation (i.e. via nitrification/denitrification) and FO membrane rejection. On the other hand, An-OMBRs and FO-anaerobic systems do not provide any biological nitrogen removal capacity. However, it is noteworthy that nitrogen removal could be achieved via struvite (i.e. magnesium ammonium phosphate) recovery, by deploying a dedicated ammonia recovery process, or by converting ammonia microbiologically into nitrous oxide for enhanced biogas utilisation [119].

The high TrOC removal capability of FO membranes is another notable advantage [120, 121]. The safe implementation of potable water reuse schemes relies on the ability of treatment processes to remove a wide range of TrOCs including, pharmaceutical residues, steroid hormones, phytoestrogens, UV-blockers, and pesticides [122-124]. In terms of FO configurations for wastewater treatment, the Ae-OMBR is likely to offer the most effective removal of TrOCs due to the combined effect of biodegradation and membrane rejection [120]. It is noteworthy that the removal of TrOCs by An-OMBRs has scarcely been reported in the literature [125].

2.3.3. Forward osmosis membrane-based hybrid systems for water recovery

Additional separation processes must be integrated with FO to recover fresh water and re-concentrate the draw solution. Key considerations for the draw solute recovery process include the ability to reject the draw solutes, draw solution compatibility with the subsequent biological treatment process, and energy requirements of the overall hybrid system. Hybrid systems that couple FO with pressure driven (e.g. NF and RO) [107, 126], thermally driven (e.g. MD) [127-129], or electrically driven (e.g. electrodialysis (ED)) [130] membrane processes have been reported in the literature (Figure 2.4). In these hybrid systems, FO pre-treats wastewater and provides a foulant-free solution for draw solute recovery. As a result, FO membrane-based hybrid systems have the potential to produce a higher quality effluent and improved process efficiency compared with treating raw wastewater directly with the above mentioned high retention membrane processes [63]. FO membrane-based hybrid systems are often termed a double-barrier defence for a wide range of contaminants.

However, as discussed in the next section, some contaminants can accumulate in the draw solution, presenting a limitation for the practical application of these hybrid systems.

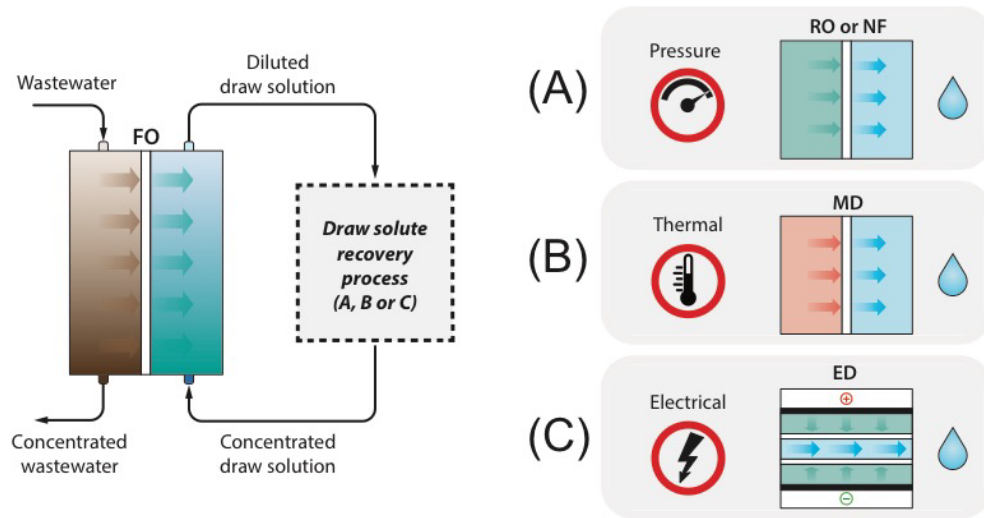


Figure 2.4. Schematic of FO membrane-based hybrid systems utilising: (A) pressure driven RO or NF, (B) thermally driven MD, and (C) electrically driven ED.

2.3.3.1. Contaminant accumulation in the draw solution

A major limitation for the practical application of FO membrane-based hybrid systems is the potential accumulation of contaminants in the draw solution. FO membranes are not completely impermeable to all dissolved solutes. Thus, contaminants that pass through the FO membrane but are retained by the draw solute recovery process inevitably accumulate in the draw solution in a closed-loop system. Previous studies have observed the accumulation of small organic compounds, ammonium, and phosphate ions using FO-RO [107] and FO-MD [97] hybrid systems. Accumulation of TrOCs has also been observed, with the type of TrOC depending on the rejection capability difference between the FO and draw solute recovery processes [97, 131].

Contaminant accumulation is an issue for the practical application of FO hybrid systems as the product water quality can be hampered and may even lead to membrane fouling in the draw solute recovery process [60, 132]. Luo et al. [107] presented evidence that the accumulation of contaminants in the draw solution of an Ae-OMBR-RO system caused an increased RO permeate concentration of organic matter and ammonium, hence, negatively affecting product water quality. Similar results were reported by D'Haese et al. [131] when they modelled TrOC accumulation in an FO-RO system. They observed TrOC build-up to a level in excess of the feed concentration which led to a contaminated product water [131]. The risk of membrane fouling in the draw solute recovery process caused by contaminant

accumulation in the draw solution has also been demonstrated. The permeability of the RO membrane in an OMBR-RO system was shown to gradually decline, suggesting that some small organic molecules can accumulate and act as foulants on the RO membrane [107]. The risk of fouling is also applicable to other draw solute recovery processes after long-term operation, unless mitigation strategies are adopted.

To safeguard the production of high quality product water and to reduce the risk of membrane fouling in FO draw solute recovery systems, additional treatment processes can be integrated to mitigate contaminant accumulation in the draw solution. The type of treatment process generally depends on the contaminant of concern. In wastewater applications, granular activated carbon (GAC) adsorption and ultraviolet (UV) oxidation have both proved to be effective processes, targeting the mitigation of organic matter and TrOCs [97]. In addition, ion exchange has been applied to the removal of accumulated boron in the draw solution of a seawater desalination process [133]. For wastewater specific applications, further research is required to address a number of practical considerations when mitigating contaminant accumulation in the draw solution. It is noted that draw solute selection can greatly impact the applicability of the applied mitigation strategy. For example, GAC and UV are not compatible with organic-based draw solutes, which can interfere with the adsorption process or be degraded by UV radiation, respectively [134].

Further research is necessary to assess the extent and impact of contaminant accumulation over long-term operation in wastewater applications using FO. Ongoing research progress in the fabrication of FO membranes can improve the rejection of target contaminants and suppress their accumulation in the draw solution [135]. Promising results have been achieved through the application of novel side-stream processes to remove contaminants from the draw solution in systems that utilise RO, NF, or MD for draw solute recovery. When ED is used for draw solute recovery, post-treatment methods may be necessary since ED has a relatively low removal capacity for organic compounds [130]. In addition, FO operating parameters can also be optimised to minimise the forward diffusion of contaminants into the draw solution.

2.3.3.2. Energy consideration for FO membrane-based hybrid systems

Energy considerations for FO membrane-based hybrid systems are of paramount importance due to the common misconceptions regarding forward osmosis as a desalination technology [136]. The FO process itself only requires minimal energy for water transport through the membrane as the draw solution provides the osmotic driving force [59].

However, it is the draw solute recovery process which dictates the energy consumption of the entire hybrid system [137]. FO based hybrid systems can utilise mechanical (i.e. pressure), thermal, or electrical energy to power the draw solute recovery process (Figure 2.4). Although the energy demand for draw solution regeneration by RO or MD is high [63], it is noteworthy that membrane fouling associated with FO wastewater treatment is highly reversible compared with direct RO [51] or MD filtration [97]. By comparison, during conventional wastewater treatment, intensive pre-treatment is required (i.e. activated sludge treatment and MF) prior to RO for potable water production. In other words, the costs associated with these conventional wastewater treatment processes could be replaced by the FO process.

The most promising avenue for FO membrane-based hybrid treatment systems to provide low energy treatment of wastewater arguably involves applications whereby low-cost heat can be utilised for draw solute recovery. MD is a thermally driven membrane process that has significant potential, since alternative low-cost or waste thermal energy can be applied to power the draw solute recovery process. It is noteworthy that in all thermally driven processes, the energy efficiency is proportional to temperature (thermal quality) [138]. Thus, the abundance of cheap or free low-grade heat is an important factor. In areas of high solar radiation, solar thermal can be used as the primary energy source. Alternatively, low-grade waste heat could be captured from nearby industrial processes. Lastly, the heat co-generated from the production of biogas from wastewater organic matter presents a practical approach to supply such thermally driven separation processes.

In terms of energy consumption, very few comprehensive comparisons of draw solute recovery processes have been reported in the literature. Life cycle analyses of FO-RO hybrid system primarily focus only on seawater desalination applications. The results were inconclusive and showed that at the current stage of FO development, FO-RO processes may have comparable costs [139] or a higher energy use and environmental impact [140] compared with current technologies for seawater desalination and water reuse. It is also noted that there has not been any life cycle analysis of FO-based hybrid system specifically for wastewater treatment applications. Further studies are crucial to practically evaluate the energy outlook of FO processes related to wastewater treatment and resource recovery applications.

Another potential opportunity to improve the energy favourability of FO systems involves the case where the diluted draw solution has a direct use, therefore no draw solute recovery

process is required. For example, the use of fertilizers as a draw solution to extract clean water for irrigation from compromised sources has been recently demonstrated. The product is a diluted fertiliser solution that can potentially be directly applied for fertigation purposes [58, 141, 142]. In these examples, water is recovered in a directly usable form. There is a similar argument for the use of seawater RO brine as the draw solution. Researchers have proposed that diluting the brine by treating wastewater with FO, and subsequently extracting water by seawater RO desalination can provide a sustainable approach to dual issues (i.e. wastewater management and fresh water availability) [143]. In some cases, it has been reported that the required energy for the combined osmotic dilution and water recovery by RO is more than a single RO process [63]. The suitability of osmotic dilution is highly dependent on local factors, however the low energy consumption of osmotic dilution is a major advantage.

2.3.3.3. Other limitations of FO-based hybrid systems

Further to contaminant accumulation and energy considerations, there are a number of inherent limitations of FO-based hybrid systems. During the process, the loss of draw solute (i.e. reverse solute flux) negatively impacts process efficiency by lowering the osmotic driving force [144]. This increases operating costs as solute must be periodically supplemented [145], and elevates salinity accumulation in the feed solution [146]. Another limitation is the low water flux of the FO process [147]. Unless significant improvements in membrane materials and draw solution efficiency are made, the capital costs associated with the required FO membrane area to compensate the low flux are extensive.

2.4. Resource recovery using forward osmosis

Extending the established efforts of wastewater treatment, FO has been recognised as a highly suitable technological building block to facilitate nutrient and energy recovery from wastewater. A number of recent studies have demonstrated the capability of FO-based processes to improve the recovery of energy and nutrients from various wastewaters (Table 2.2). Some of these FO-based processes are able to recover resources whilst simultaneously providing wastewater treatment when coupled with a draw solute recovery process. Despite these promising demonstrations of simultaneous wastewater treatment and resource recovery by FO-based processes, a number of key technical challenges require further development. More research is needed to optimise the integration of FO with anaerobic processes for biogas production, to overcome issues of salinity accumulation and membrane fouling. Also,

it is necessary to focus efforts on developing nutrient recovery using FO to address the key issues of product purity and membrane fouling/scaling during long-term operation.

2.4.1. Integrating forward osmosis with anaerobic treatment for biogas production

Integrating the FO process with anaerobic treatment is a promising avenue to produce biogas and recover nutrients from wastewater. Two distinct approaches include the An-OMBR configuration or direct FO pre-concentration followed by an anaerobic digester. Demonstrations of FO-based systems producing biogas have focused almost exclusively on An-OMBRs, where the FO membrane is submerged within the anaerobic bioreactor (Table 2.2). Recent research has reported the potential of An-OMBRs as methane yields between 0.2 and 0.3 L CH₄/g COD were achieved in lab-scale studies [54, 56]. Compared to conventional anaerobic digesters, the inclusion of the FO membrane can provide a number of important advantages. Firstly, the treatment performance of An-OMBRs surpasses conventional anaerobic systems in terms of organic matter and nutrient removal [28, 58]. FO membrane separation also allows the system to operate at a high organic loading rate by decoupling the hydraulic retention time and the solid retention time, hence, lowering the process footprint [148]. Lastly, potable water production is enabled by adopting an appropriate draw solute recovery process for the draw solution.

An alternative approach that could essentially achieve the same objective as An-OMBRs involves directly processing primarily treated wastewater by FO and then feeding the concentrate to an anaerobic treatment system. A key advantage of this configuration (Figure 2.3C) is that the FO membrane is in contact only with wastewater, which is more dilute than sludge. Sun, et al. [149] reported that fouling reversibility was higher in a direct FO system compared to an OMBR, attributed to differences in the solutions microbiological behaviour [103]. Similarly, membrane degradation may be less severe in direct FO configurations, as prolonged exposure to activated sludge in OMBRs has shown to result in significant performance degradation to both cellulose triacetate (CTA) and thin film composite (TFC) FO membranes [150]. Furthermore, the volumetric loading of the anaerobic treatment system could be drastically reduced, owing to the pre-concentration of wastewater by the FO membrane. Enriching the COD concentration of wastewater has the potential to increase the energy recovery per unit volume of digestate and to minimise digester heating energy requirement [111]. Detailed studies are needed to assess the pre-concentration capability of FO as well as to demonstrate the process performance and challenges.

Table 2.2. Summary of FO-based resource recovery processes.

Feed solution	FO-based process	Recovered resource	Draw solution	Draw solute recovery process	Performance	Ref.
Synthetic wastewater	An-OMBR	Biogas	NaCl	Manual re-concentration	Methane yield = 0.21 L CH ₄ /g COD	[54]
	An-OMBR	Biogas	NaCl	Manual re-concentration	Methane yield = 0.3 L CH ₄ /g COD	[56]
	An-OMBR	Biogas	NaCl and Na ₂ SO ₄	Manual re-concentration	NaCl An-OMBR had a higher biogas methane composition than Na ₂ SO ₄ An-OMBR	[57]
Activated sludge	Ae-OMBR	Calcium phosphate	MgCl ₂ and NaCl	Manual re-concentration	Phosphorus content >11%	[108]
	MF-Ae-OMBR	Calcium phosphate	Seawater brine	Osmotic dilution	MF extracted dissolved nutrients. Phosphorus content = 11–13%	[151]
	MF-Ae- OMBR-RO	Calcium or magnesium phosphate Fresh water	NaCl	RO	Precipitate = 15-20% phosphorus	[107]
Secondary treated effluent	FO pre-treatment	Nutrient concentrate (i.e. ammonia and phosphate)	Synthetic seawater	Osmotic dilution	Ammonia removal = 66.7% Phosphate removal = 92.1	[114]
Digested sludge centrate	FO-RO	Nutrient concentrate (i.e. ammonia and phosphate) Fresh water	NaCl	RO	Ammonia removal =82.9–92.1 % Phosphate removal=99.6–99.9% Optimum water recovery=70% Ammonium removal >90%	[30]
	FO-MD	Struvite (MgNH ₄ PO ₄ ·6H ₂ O) Fresh water	MgCl ₂	MD	Phosphate removal >97% Bidirectional diffusion of Mg ²⁺ and protons improved struvite recovery.	[152]
Urine	FO pre-treatment	Nutrient concentrate (i.e. ammonium, phosphate, and potassium)	Synthetic seawater and brine	Osmotic dilution	Ammonium removal = 50–80% Phosphate removal > 90% Potassium removal >90%	[118]

The primary purpose for considering anaerobic treatment for wastewater treatment is to recover the chemical energy contained in wastewater through biogas conversion. In the proposed FO-based process (Figure 2.5), biogas produced from the anaerobic treatment process has significant potential to supply the energy requirements of the system. In this case, MD presents a favourable opportunity for draw solute regeneration, as the driving force of MD is temperature. A combined heat and power engine can convert biogas into heat for the MD system. Furthermore, electricity can be utilised onsite or fed back into the grid. According to an energy audit of the Prague WWTP, under an optimal condition, 70–80% energy self-sufficiency could be achieved by fully utilising the embedded chemical energy in wastewater for biogas production [153]. Thus, energy self-sufficiency is possible with further improvement in engineering efficiency. Lastly, anaerobic treatment partially mineralises organic nitrogen and phosphorus to their soluble forms (i.e. ammonium and phosphate). This action increases the chemical availability of nutrients for subsequent recovery. Despite these benefits, the major technical challenges that limit the feasibility of integrated FO and anaerobic treatment systems are salinity accumulation and membrane fouling.

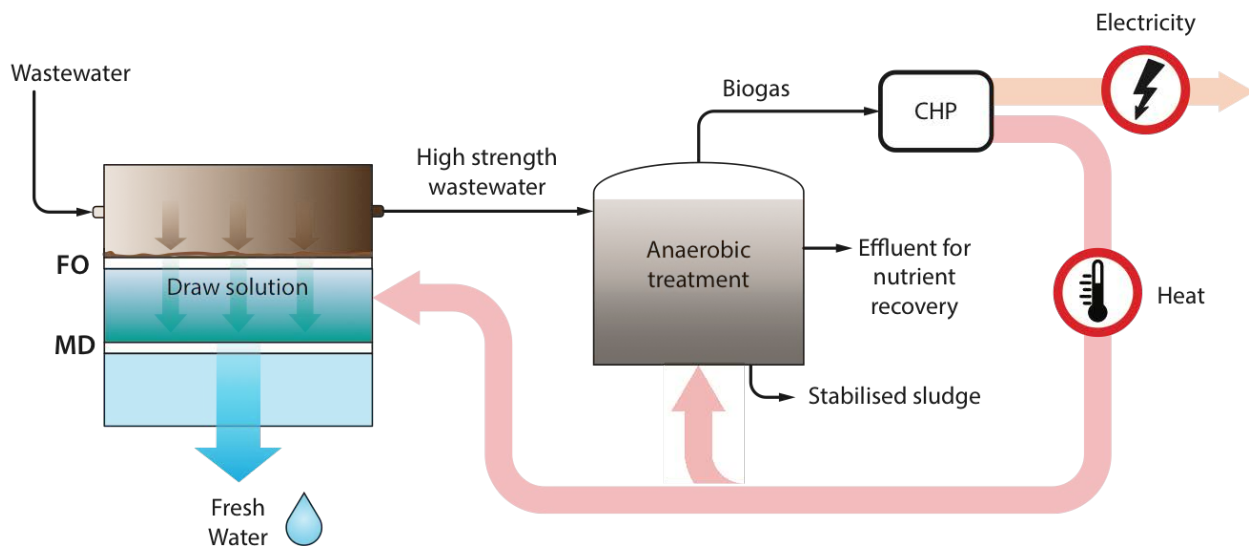


Figure 2.5. Schematic of an FO pre-concentration process for energy recovery via anaerobic treatment.

2.4.1.1. *Salinity accumulation*

Salinity accumulation is a prevalent issue for the integration of high retention membrane processes with biological treatment [49]. For FO, this issue is further exacerbated by the reverse diffusion of solutes from the draw to the feed solution (i.e. reverse draw solute flux). The accumulation of salt in the feed solution inevitably increases its osmotic pressure and can negatively impact water flux. More importantly, salinity accumulation is a major hindrance when integrating FO with anaerobic treatment since methanogenic activity can be inhibited at high inorganic salt concentrations, leading to severely reduced biogas production rates [24]. It is noteworthy to mention that methane solubility decreases as salinity increases [154]. This could be beneficial in terms of reducing methane loss via permeate. The extent of salinity accumulation and the impact on water flux and anaerobic treatment is strongly affected by the selected draw solution and the FO operating conditions (i.e. concentration factor). The relative contribution of each salinity accumulation mechanism can be predicted based on the operating conditions and draw solute properties [146, 155]. For this application whereby organic loading rates should be increased, the FO concentration factor must be maximised. Yet, the concentration factor is proportional to the rate of salinity build-up and therefore a trade-off exists between the effects of salinity accumulation and process efficiency. Thus, a variety of strategies have been proposed to alleviate salinity accumulation in FO-based systems.

The draw solution significantly influences both the rate of reverse draw solute flux and the type of solutes that accumulate in the feed solution [74, 144]. Feasibility studies have shown that the use of sodium chloride as the draw solution in An-OMBRs inevitably leads to severe salinity accumulation that detrimentally affects water flux and system efficiency [54, 56]. Furthermore, the accumulation of both sodium chloride and sodium sulphate draw solutes significantly impacted growth of methanogens in An-OMBRs [57]. One approach to mitigate this problem is to utilise alternative draw solutes (Figure 2.6A). Overall, ionic organic draw solutes such as sodium acetate (NaOAc) and ethylenediaminetetraacetic acid (EDTA) based salts hold the greatest promise. The reverse solute flux of NaOAc and EDTA-2Na are reported to be 70% and 86% lower than sodium chloride, respectively, which reduces the rate of salinity accumulation and draw solute replenishment [156]. The use of ionic organic draw solutes has been demonstrated in lab-scale Ae-OMBRs and has shown excellent mitigation of salinity build-up in the reactors [127, 134]. In terms of anaerobic treatment, no demonstrations of alternative draw solutes have been reported, therefore there is a need to

develop a draw solution selection criterion specifically for FO processes that integrate anaerobic treatment. Importantly, the risk of methanogenic inhibition as a result of reverse draw solute flux and the potential biogas enhancement from organic draw solutes requires evaluation.

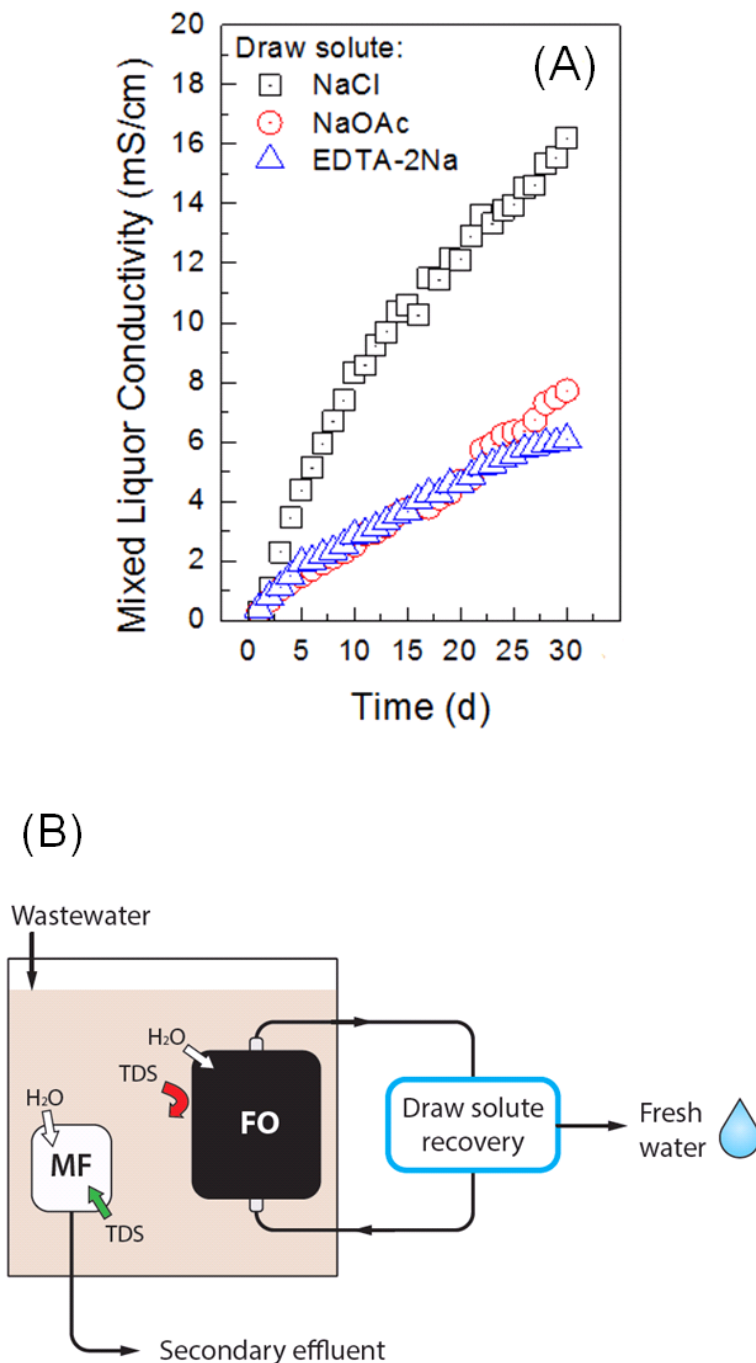


Figure 2.6. Mitigation of salinity accumulation by (A) alternative draw solutions for Ae-OMBR [134] and (B) MF withdrawal of total dissolved solids (TDS) in an OMBR (adapted from Qiu et al. [151]).

The high cost of ionic organic draw solutes remains an important barrier for the practical implementation of these FO draw solutions. For this reason, a number of recent demonstrations of FO integrated anaerobic systems have generally adopted lower cost sodium chloride or seawater as the draw solution and relied on non-optimal operating conditions, such as excessive sludge wastage or periodic supernatant discharge in order to avoid the effects of salinity build-up on the process [54, 56]. Although these studies present the feasibility of biogas production (i.e. 0.2–0.3 L CH₄/g COD) via the An-OMBR process, conditions are unrealistic and are not a practical long-term solution to salinity accumulation. A proof of concept which can potentially lead to a full-scale sustainable option for salinity mitigation involves the integration of an MF membrane within an Ae-OMBR [151, 157]. The MF membrane acts as a bleeding stream since dissolved solutes can easily pass through the MF membrane (Figure 2.6B). This integrated system manages to sustain the FO process, whilst at the same time produces MF quality effluent for reuse applications requiring lower water qualities. Similar benefits may also be realised if MF is integrated with An-OMBR, however this approach would result in the partial loss of organic substances.

Another promising approach involves acclimatising the anaerobic microbial community to saline environments. In anaerobic systems, microorganisms are able to tolerate high salt conditions if acclimated to the conditions [158, 159]. Indeed, the anaerobic treatment of high saline industrial wastewater is feasible with adequate biomass adaption or by using halotolerant organisms [160]. Further research on identifying and implementing certain halotolerant bacteria in an anaerobic system would be significantly beneficial to developing FO-based anaerobic systems. The presence of halotolerant organisms would allow the FO system to operate at a higher concentration factor. Furthermore, when draw solutions with a low reverse solute flux are applied, the negative impacts associated with salinity accumulation on biogas production would be circumvented. Overall, a greater focus is required to assess and advance the practicality of FO-based systems that integrate anaerobic treatment for biogas production. A combination of the previously mentioned strategies in a pilot-scale system would significantly contribute to assessing their long-term effectiveness, and is imperative to improving our understanding of FO-based anaerobic systems.

2.4.1.2. Membrane fouling

Although FO membrane fouling is readily reversible, fouling remains a pertinent issue for FO-based processes applied to complex solutions such as wastewater and mixed liquor [103, 132, 161]. During filtration, the accumulation of foulants on the membrane surface forms a

cake layer and hinders the efficiency of the process by two predominant mechanisms. The cake layer builds hydraulic resistance and also creates the cake-enhanced concentration polarisation effect that lowers the osmotic driving force. Both of these mechanisms adversely impact membrane performance by decreasing water flux and membrane life-span [63, 103]. Various approaches have been demonstrated to manage membrane fouling. These include physical and chemical cleaning methods, as well as modification of membranes to be fouling resistant.

A key benefit of the FO process when applied for wastewater pre-concentration is the highly reversible nature of membrane fouling compared to other pressure driven membrane processes. Therefore, membrane fouling control can often be accomplished by hydraulic means, whereby hydrodynamic shear forces are introduced to prevent the accumulation of foulants near the membrane surface [80, 92]. This method is not possible when using pressure driven membrane processes for direct wastewater treatment since fouling cannot be removed without chemical cleaning. Hydrodynamic strategies including periodic rinsing at high cross-flow velocities, inclusion of spacers, and air sparging via biogas recycling, have proved effective in wastewater treatment applications [54, 92, 162]. Despite these results, the intensity of the fouling control strategy inevitably leads to heightened energy consumption. Therefore, a significant focus should be placed on evaluating and optimising the energy consumption of proposed fouling mitigation strategies. It is also necessary to develop a membrane cleaning protocol specifically for intense wastewater pre-concentration applications by FO membranes.

2.4.1.3. Issues arising from the anaerobic treatment of FO pre-concentrated wastewater

In addition to the key challenges of salinity accumulation and membrane fouling, a range of other issues may arise as a result of the anaerobic treatment of FO pre-concentrated wastewater. Inorganic salt inhibition and ammonia toxicity may plague the efficiency of the anaerobic treatment process, regardless of mitigation strategies. In this case, the co-digestion of readily available organic substrates (i.e. food waste or industrial by-products) could significantly improve the digester efficiency [163, 164]. Furthermore, phosphorus may precipitate in the anaerobic reactor due to the enriched content of phosphorus, calcium, and magnesium in the pre-concentrated wastewater [54]. This may lead to complications for phosphorus recovery, as the availability of phosphorus in the liquid phase would be limited. However, this scenario could be easily avoided by acidifying the pre-concentrate. Conventional MF An-MBR is an ideal candidate for biogas production from the pre-

concentrated wastewater. In addition, the ammonia and phosphorus rich supernatant (i.e. anaerobic digestion effluent) can be withdrawn via the MF membrane for subsequent recovery.

Studies to date have focused almost exclusively on the integration of FO and anaerobic treatment to form An-OMBRs [54, 56, 57] or to filter anaerobic effluent [165-167]. Therefore, there is a significant gap in current knowledge regarding the anaerobic treatment of FO pre-concentrated wastewater.

2.4.2. Nutrient recovery

The rejection of nutrients by FO membranes results in high quality product water, and can also facilitate the removal and recovery of nutrients from wastewater. Phosphorus in particular has significant environmental value and is consistently highly rejected by FO membranes from a range of different feed solutions and operation conditions (Table 2.1). In recent years, there has been a significant growth in nutrient recovery research using FO-based processes [39]. Phosphorus recovery from a number of diverse source waters, including waste activated sludge [107, 108, 151], secondary treated effluent [114], digested sludge centrate [30, 152], and urine [118] has been demonstrated in the literature. Several FO-based configurations have been used including Ae-OMBR and direct FO filtration. Overall, FO is utilised to firstly concentrate nutrients, and then conventional nutrient recovery techniques are applied to chemically precipitate phosphate minerals (Table 2.2).

FO has several features that are ideal for nutrient recovery from wastewater. Firstly, FO membranes can effectively retain phosphorus, thus enriching its concentration and providing favourable conditions for phosphorus recovery. As an example, struvite recovery requires the addition of magnesium and ammonium ions to exceed the stoichiometric ratio for struvite precipitation. Thus, the phosphorus rich solution provided by the FO process improves precipitation kinetics and lowers the chemical demand (i.e. magnesium salts and caustic). Secondly, the reverse solute flux (which is usually seen as problematic in FO) can be utilised for nutrient recovery applications. Xie et al. [152] strategically utilised $MgCl_2$ as a draw solution to enrich the magnesium content of the feed solution via the reverse magnesium flux mechanism. Lastly, the bidirectional diffusion of solutes in the FO process enables the feed solution pH to naturally increase. Several researchers have observed this bidirectional transport phenomenon. In particular, Xie et al. [152] has demonstrated the direct benefit of the bidirectional transport of Mg^{2+}/Ca^{2+} and proton (H^+) for struvite precipitation.

There are a number of configuration options for FO-based systems for nutrient recovery. Ae-OMBRs treating dilute wastewater have demonstrated excellent potential for nutrient enrichment within the mixed liquor or by supernatant withdrawal [108, 151, 168] (Figure 2.7A). Also, direct pre-concentration processes applied to anaerobic digestion effluent has provided some promising results as this system could be easily integrated with current wastewater treatment infrastructure [152]. In terms of nutrient recovery efficiency, the direct pre-concentration of anaerobic effluent (i.e. digested sludge centrate) is possibly the most viable approach as there is minimal loss of nutrients caused by biomass uptake, as is the case in Ae-OMBRs. In aerobic processes, nutrients are consumed or converted by activated sludge, therefore, a lower theoretical amount of phosphorus is available for recovery. Conversely, anaerobic treatment biologically releases nutrients, transforming them into more chemically available forms for precipitation (Figure 2.7B). Investigations into FO performance when treating nutrient rich solutions are increasing [165-167], however there are still several key aspects to be addressed. These include membrane fouling and scaling, precipitate purification, and issues related to the market development for bio-fertilizers produced from wastewater.

Membrane scaling could be a prominent barrier for FO application to nutrient recovery, however, this has not been previously investigated. It is important to consider the possibility of membrane scaling during resource recovery as it dramatically affects process performance and chemical cleaning is often required, resulting in a decreased membrane life-span. The super-saturation of phosphate minerals close to the membrane surface may lead to the precipitation of salts onto the membrane surface. Research to date has not identified any significant problems associated with membrane scaling during nutrient recovery applications. This is likely due to the short term nature of the proof of concept studies in the current literature. Pilot-scale evaluation and modelling are required to assess the risk of membrane scaling for nutrient recovering FO processes and develop efficient chemical cleaning protocols. In addition to membrane scaling, the presence of calcium and phosphate in the FO feed solution can lead to cake layer formation [169]. Nevertheless, membrane flushing has been reported to be an effective strategy to remove cake formation [152].

One key advantage for nutrient recovery is the potential profit obtained from the sale of the bio-fertilizers produced. However, a market for fertilisers sourced from wastewater is currently not well-defined. The product value largely depends on the purity of the product obtained. At this stage, product purity has not been a significant area of research for the previously mentioned FO-based nutrient recovery systems. For example, for calcium

phosphate recovery, the competition of calcium and magnesium for phosphate and the presence of organic matters can drastically degrade product quality [151]. There is significant potential for FO-based processes to be further integrated with established resource recovery techniques. These may include the introduction of seed crystallisation [170] or by further purification of FO pre-concentrated nutrient solutions by technologies such as ED [39].

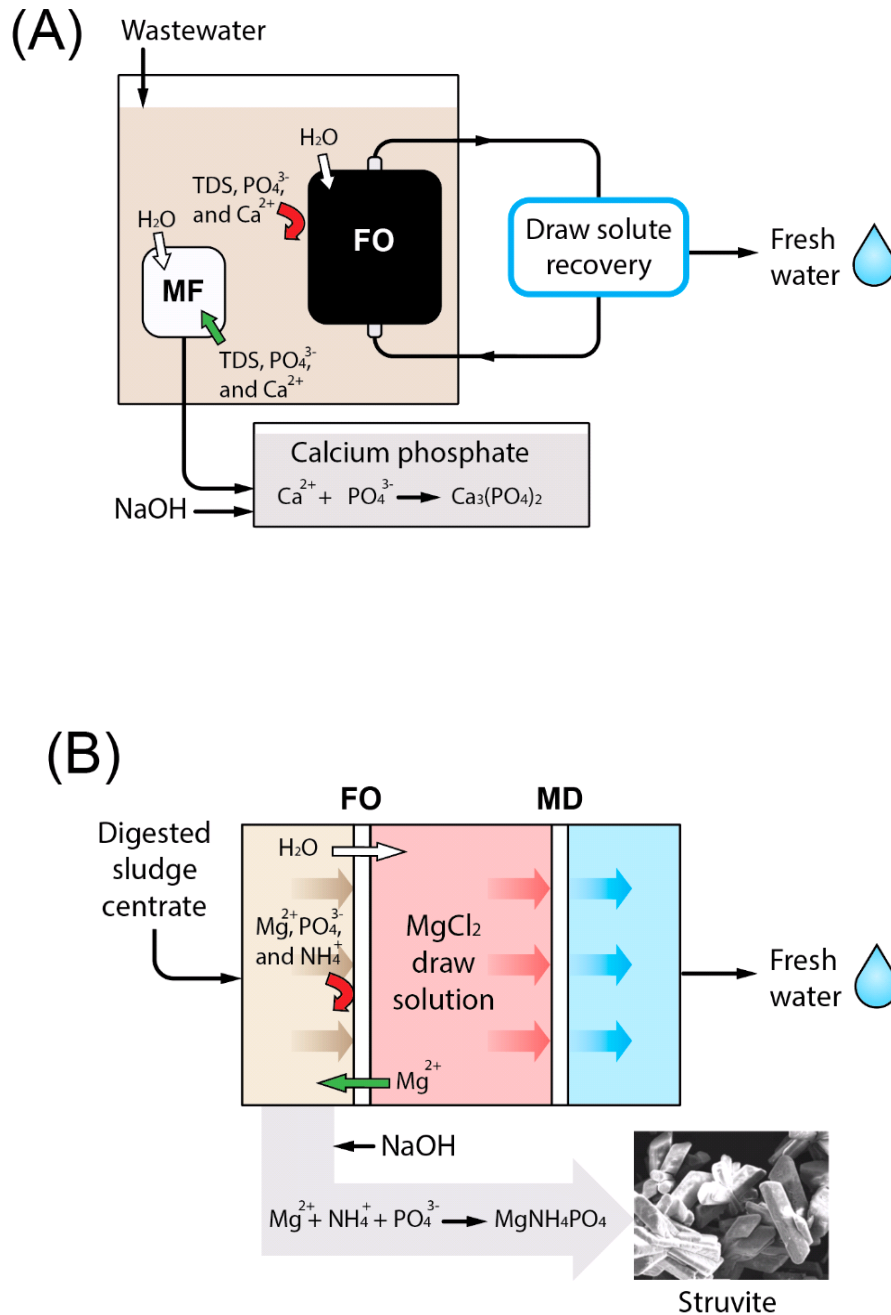


Figure 2.7. Phosphorus recovery using (A) MF withdrawal from Ae-OMBR mixed liquor (adapted from Qiu et al. [151]) and (B) FO-MD of anaerobically digested sludge centrate (adapted from Xie et al. [152]).

2.5. Integrated wastewater treatment and resource recovery process

Based on current FO research and development, an integrated FO-based wastewater treatment and resource recovery process is proposed and compared with current wastewater treatment practices (Figure 2.8). Current wastewater treatment (Figure 2.8A) is highly energy intensive, with aeration and pressurised membrane systems being significant energy consumers. The process also focuses strictly on water reclamation and does not effectively integrate energy and nutrient recovery practices. Although sludge is often anaerobically treated, a large portion of the chemical energy in wastewater is dissipated by the initial aerobic biological process [46].

Unlike current wastewater treatment practices, the proposed FO-based process (Figure 2.8B) focuses on the separation of water and non-water components to enable more efficient resource recovery. In this process, primarily treated effluent is firstly filtered by the FO process coupled with MD to produce high quality effluent for reuse. Ionic organic draw solutes are employed to minimise reverse draw solute flux, and to lower the risk of methane inhibition during anaerobic digestion. The FO pre-concentrate is fed to an anaerobic digester to produce biogas. A combined heat and power system converts biogas to useful heat for operating MD, and electricity for treatment operations. Furthermore, nutrient rich anaerobic effluent is processed by an FO-MD system to further harvest valuable nutrients for subsequent recovery. Struvite recovery can be achieved using $MgCl$ as the draw solution [152], whilst calcium phosphate can be recovered using seawater [152]. This MD system would also produce high quality effluent for reuse, which is a significant benefit, as anaerobic effluent is commonly returned to the headworks in conventional treatment plants. For these reasons, FO can potentially serve as a game changer in municipal wastewater treatment.

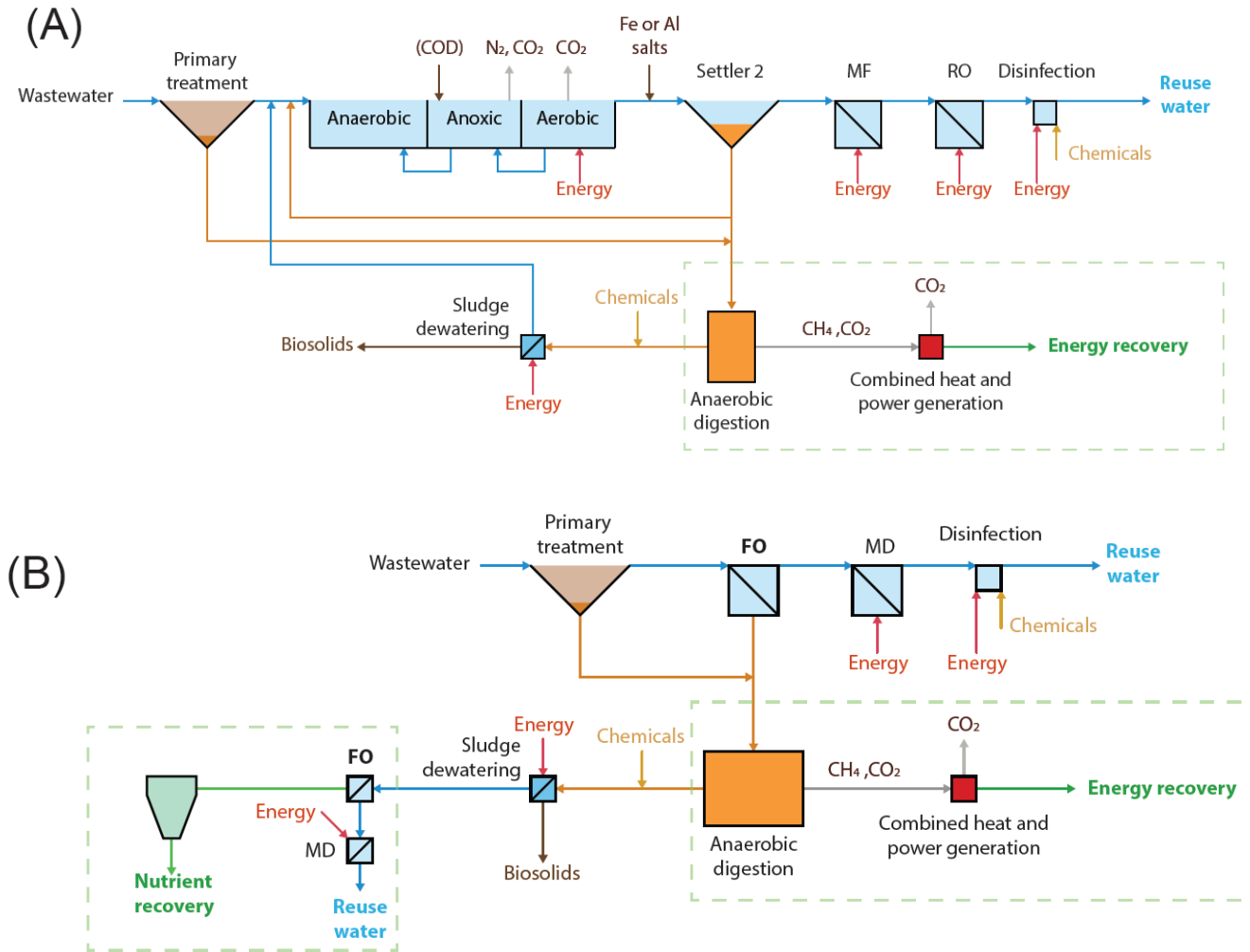


Figure 2.8. Comparison of current and FO-based wastewater treatment technologies. (A) Current processes consume significant energy, dissipate wastewater organic matter, and do not effectively manage nutrients (adapted from Verstraete et al. [45]). (B) The proposed FO-based treatment process achieves simultaneous wastewater treatment and resource recovery, utilising produced energy within its operations and recovering nutrients.

2.6. Outlook

FO-based processes have a proven capability and offer a unique opportunity to achieve simultaneous wastewater treatment and resource recovery. Yet, FO technology is still in the early stage of development and therefore the realisation of full-scale implementation will continue to evolve as the field becomes more mature. Two important considerations for this concept include the applicability of FO-based systems to a decentralised or centralised level and economic barriers that strongly affect the acceptance of the technology.

Issues regarding the scale-up of FO based processes involve the inherently low water flux of the FO process. Low water flux corresponds to a large footprint which substantially increases capital and operational costs. Considering the direct filtration of raw wastewater by FO, with the current state of FO membranes, environmental and economic benefits may only be realised for decentralised applications. This is due to the significantly large volumetric loading of centralised wastewater treatment systems in urban areas. Furthermore, there is an increasing drive to house treatment facilities onsite or nearby to the water reuse locations (i.e. farming areas or industrial areas) [171]. This concept of sewer mining strategically avoids the energy needed to convey reuse water from a centralised WWTP, however quality control would be an added issue to be addressed. Further investigations to assess the feasibility of FO scale-up must be conducted in terms of both technical and economic viability. In the future, improvements of FO membrane materials, module design, draw solutions, and draw solute recovery processes may provide practical opportunities for the scale-up of FO systems at a centralised level.

Regarding nutrient recovery using FO-based technology, important advantages are likely to be realised sooner as the process can be integrated with current wastewater treatment infrastructure (i.e. treating anaerobically digested sludge centrate). Furthermore, nutrient recovery presents a practical business case for struvite blockage prevention, phosphorus effluent discharge compliance, and fertilizer production potential [3]. In fact, struvite recovery has been demonstrated at several full-scale WWTP in North America [172]. We envisage that FO can greatly improve the process efficiency and therefore break-down some of the economic barriers that prevent nutrient recovery being an established practice [173].

Resource recovery from municipal wastewater presents a promising opportunity for a number of contemporary environmental challenges. However, several economic barriers exist and restrict the acceptance and implementation of such practices. The environmental value of

water, energy, and nutrient resources cannot be readily captured by current economic analysis. This is illustrated by the availability of low cost electricity, natural gas, and mineable phosphorus that strongly resist investment appeal. Furthermore, the lack of a well-defined market for saleable bio-fertilizers may influence the acceptance of nutrient recovery technologies. Nonetheless, resource recovery from wastewater represents a renewable source of water, energy, and nutrients. Particularly when considering how population growth and urbanisation will continue to stress non-renewable resource reserves in the future. The introduction of government incentives may provide a profound milestone in implementing resource recovery practices. Further investigations into the economic feasibility of technologies that enable resource recovery from wastewater should be a high priority.

2.7. Conclusion

The FO process is a favourable avenue to advance a membrane-based platform to achieve simultaneous wastewater treatment and resource recovery. FO membranes can be applied to a complex and high fouling solution and retain a wide range of contaminants. FO membrane-based hybrid systems that combine FO with a draw solute recovery process (i.e. MD) effectively enable fresh water recovery from wastewater. Extending this effort, energy and nutrient recovery from wastewater can be initiated through the strategic integration of FO with anaerobic biological treatment. FO membranes can successfully pre-concentrate wastewater and improve the organic loading rate of anaerobic treatment systems for biogas production. Similarly, the FO process can harvest valuable nutrients within anaerobic effluent, and significantly benefit the efficiency of established phosphorus recovery techniques.

Despite the potential of FO to emerge as an important membrane technology in the future, several major technical challenges still remain. These include contaminant accumulation in the draw solution, salinity accumulation, membrane fouling, and anaerobic system integration. A number of innovative approaches can be utilised to resolve these challenges as highlighted in this review. Further development of the practical aspects of this concept via pilot-scale demonstrations is recommended. One major milestone in the development of FO technology for this application involves the successful demonstration of integrated FO and anaerobic treatment systems. Furthermore, energy considerations for the proposed process must also be clearly dictated through techno-economic assessments that address the likely advantages of the process compared with current technologies. Issues associated with the scale-up of FO-based processes at a decentralised or centralised level must also be addressed.

Development of FO membrane materials and anaerobic microbial selection techniques are expected to strongly benefit research progress towards FO-based technology for simultaneous wastewater treatment and resource recovery.

CHAPTER 3: Selection of forward osmosis draw solutes for subsequent integration with anaerobic treatment to facilitate resource recovery from wastewater

Corresponding publication:

A.J. Ansari, F.I. Hai, W. Guo, H.H. Ngo, W.E. Price and L.D. Nghiem, Selection of forward osmosis draw solutes for subsequent integration with anaerobic treatment to facilitate resource recovery from wastewater, Bioresource Technology, 191 (2015), 30-36.

3.1. Introduction

The recently recognised value of clean water, energy, and nutrients in municipal wastewater has led to a paradigm shift in urban water management, toward a modern framework that incorporates resource recovery with the traditional sanitation mandate. The value of these resources goes beyond short-term economic outcomes, because long-term human health and environmental benefits can play an even greater role in wastewater management decisions. Water scarcity and environmental pollution have driven water reuse to become an integral function of modern wastewater treatment plants [6]. Further efforts to include energy and nutrient recovery are justified by the relationship between the stringency of effluent regulations and energy consumption [174], as well as concerns for worldwide phosphorus security [36].

Clean water reclamation from municipal wastewater is well established. However, a greater focus is required to further develop energy and nutrient recovery practices. The dilute nature of municipal wastewater is a major obstacle hindering energy and nutrient recovery. Thus, it is necessary to pre-concentrate municipal wastewater by five- to ten-fold to achieve the required strength in terms of chemical oxygen demand (COD) for subsequent anaerobic treatment [45], through which energy and nutrients can be recovered in the form of biogas [175, 176] and struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) [152, 177], respectively. The most common technique to recover nutrients after anaerobic treatment is via struvite precipitation. In this process, magnesium salt addition is required for struvite formation. However, because of the low ammonium and phosphate concentrations in municipal wastewater, magnesium salt must be added to obtain a concentration well above the stoichiometric ratio to facilitate struvite precipitation. In this instance, the pre-concentration of wastewater will lower the magnesium

requirement for struvite formation [22, 152], thus significantly improving the economics of nutrient recovery [177]. The deployment of innovative technologies such as forward osmosis (FO) to pre-concentrate organic matter and nutrients can facilitate anaerobic treatment, thus allowing resource recovery to become economically viable.

FO is a promising technology for the pre-concentration of wastewater and has recently demonstrated potential for direct sewer mining [97, 112]. When applied directly for wastewater treatment, this concentration driven process has several significant advantages, including a high rejection of contaminants and low fouling propensity compared to pressure driven microfiltration. Therefore, FO can concentrate the organic matter and nutrients in wastewater to a small volume for potential integration with anaerobic treatment to facilitate resource recovery. Furthermore, FO provides robust pre-treatment for reverse osmosis [178] or membrane distillation [97] for clean water production.

Reverse solute flux is an inherent phenomenon in FO. When integrating FO with a bioreactor, a major technical challenge is the migration of draw solute into the mixed liquor. This can severely affect the biological performance, particularly of the anaerobic treatment process as inhibitory substances are often the major cause of instability and failure of anaerobic treatment systems [179]. Inorganic salts are widely used as draw solutes for FO, since they are usually inexpensive, capable of generating high osmotic pressures, and are less likely to induce significant internal concentration polarization (ICP). ICP associated with inorganic salts is low because of their small solute size and rapid diffusion; however, these properties often promote a high reverse solute flux [63]. For example, sodium chloride has a high reverse solute flux, and therefore sodium concentrations are likely to exceed the value known to inhibit anaerobic treatment (3 g Na/L) [159] during wastewater pre-concentration.

Several draw solutes have been investigated with the intention of avoiding or reducing the effects of reverse solute flux on subsequent biological treatment. Lutchmiah, et al. [180] demonstrated that zwitterionic compounds, such as glycine, have a lower reverse solute flux compared to sodium chloride and the potential to increase the methane yield of concentrated wastewater due to their osmoprotectant properties. Bowden, et al. [156] proposed ionic organic salts as substitute draw solutes in osmotic membrane bioreactors (OMBRs), whereby salt accumulation has detrimental effects on biological performance. Other approaches involve comparing the microbial toxicity of draw solutions [181] or the long-term operation of alternative draw solutions in OMBRs to evaluate effects [182]. Nonetheless, no studies have evaluated the potential impact of reverse solute flux on subsequent anaerobic treatment.

This is despite the availability of the well-established biomethane potential (BMP) test, which can be used to simulate the anaerobic treatment process in batch mode to assess the methane production from different substrates [183-185].

In this chapter, a draw solute selection protocol was developed for FO systems which are integrated with anaerobic treatment. FO flux performance was assessed based on water flux and reverse solute flux. The effect of reverse solute flux on anaerobic treatment was evaluated by BMP analysis of draw solute-impacted substrate.

3.2. Materials and methods

3.2.1. Preliminary draw solution selection protocol

A literature review of previous FO studies to pre-concentrate wastewater was conducted to select ten draw solutions to undergo experimental assessment. Firstly, organic draw solutions that have demonstrated a suitably high water flux and the expectation to have negligible impact on anaerobic treatment were considered. Secondly, inorganic draw solutions with low reverse solute flux were considered and sodium chloride was selected as a reference. OLI Stream Analyzer (OLI Systems, Inc., Morris Plains, New Jersey, USA) was then used to simulate osmotic pressure as a function of draw solution concentration, to verify the suitability for further FO experimental assessment and biological screening.

3.2.2. Materials and chemicals

Cellulose triacetate (CTA) membrane with embedded polyester screen support was acquired from Hydration Technologies Innovation (HTI) (Albany, Oregon, USA). Digested sludge was obtained from a full-scale wastewater treatment plant (Wollongong, Australia) and was used as inoculum for the BMP measurements. All draw solutes used in this study were of analytical grade.

3.2.3. Forward osmosis system

FO experiments were conducted using a lab-scale, cross-flow FO membrane system (Figure 3.1). The FO membrane cell consisted of two symmetric flow channels each with length, width, and height of 130, 95, and 2 mm, respectively, and an effective membrane area of 123.5 cm².

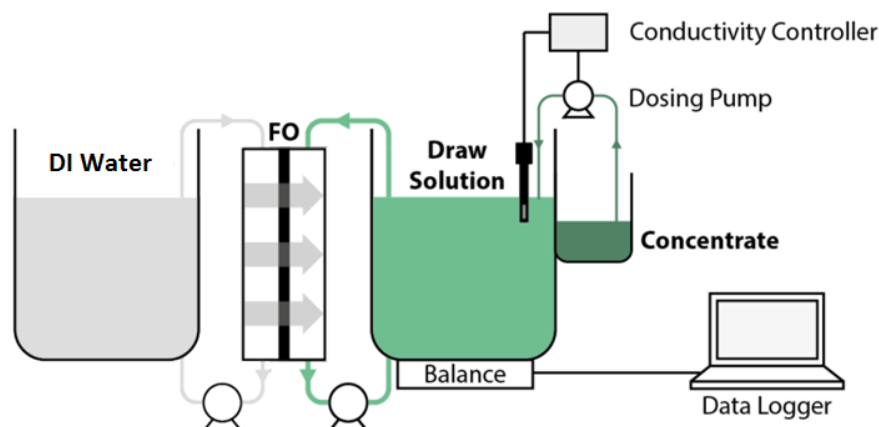


Figure 3.1. Schematic diagram of the laboratory-scale FO system.

The feed and draw solutions were circulated by two variable speed gear pumps (Micropump, Vancouver, Washington, USA) at 1 L/min (corresponding to a cross-flow velocity of 9 cm/s) and was regulated by two rotameters. The working volumes of the feed and draw solution reservoirs were 3 and 2 L, respectively. The draw solution reservoir was positioned on a digital balance (Mettler-Toledo Inc., Hightstown, New Jersey, USA) and weight changes were recorded to determine permeate water flux. For ionic draw solutions, a reservoir containing a highly concentrated solution was also placed on the digital balance and was intermittently dosed into the draw solution to maintain constant osmotic pressure. The conductivity of the draw solution was continuously measured by a conductivity probe (Cole-Parmer, Vernon Hills, Illinois, USA), which was connected to a controller (control accuracy of ± 0.1 mS/cm) and a peristaltic pump to automatically regulate the draw solution concentration. For the neutral (covalent) organic draw solutions, concentration was manually controlled by adding the correct volume of highly concentrated solution every 2 h.

3.2.4. Forward osmosis assessment

The flux performance of each draw solution was evaluated by using the lab-scale, cross-flow FO system to determine water flux (J_w) and reverse solute flux (J_s). FO experiments were conducted according to the standard procedure previously described by Cath, et al. [186]. Analytical grade solutes were dissolved in DI water at concentrations corresponding to an osmotic pressure of 30 bar. This osmotic pressure was selected for two reasons. Firstly, seawater has an approximate osmotic pressure of 30 bar and could be used as a readily available and inexpensive NaCl solution. Secondly, higher osmotic pressures were not investigated due to the corresponding increase in draw solute viscosity (particularly for

organic and/or high molecular weight solutes) and the expected exacerbation of ICP. Each draw solution was tested in FO mode (active layer facing the feed solution) with DI water as the feed solution. Conductivity, pH, and temperature of the feed solution were monitored hourly. For the covalent organic draw solutions, a 20 mL sample was withdrawn from the feed solution every 2 h for subsequent total organic carbon (TOC) analysis. All FO experiments were conducted in duplicate and lasted for at least 6 h.

Reverse solute flux selectivity (RSFS) describes the volume of permeate water per gram of solute that has diffused from the draw solution to the feed solution and can be expressed as (J_w/J_s). RSFS is important for draw solution selection in terms of replenishment costs, yet this parameter can more importantly give an indication of the expected solute concentration in FO concentrate. The draw solute concentration in the pre-concentrated wastewater (C_f) was calculated using Equation 3.1.

$$C_f = \frac{1}{(J_w / J_s)} \cdot \frac{R}{1 - R} \quad \text{Equation 3.1}$$

Where J_w/J_s is the RSFS observed during the FO performance experiments, and R is the assumed FO system water recovery. Equation 3.1 is based on the premise that flux decline (due to membrane fouling or an increase in feed solution osmotic pressure) is negligible and that RSFS is constant. A system water recovery of 90% was used to represent a ten-fold increase in the strength of municipal wastewater by FO pre-concentration. This condition can also be used to represent the worst-case scenario with respect to the impact of draw solutes on potential anaerobic treatment of the pre-concentrated wastewater.

3.2.5. Biomethane potential apparatus and protocol

BMP measurements were conducted to indicate the effect of each draw solute on methane production during anaerobic digestion. The BMP apparatus could simultaneously deploy up to 16 fermentation bottles, which were submerged in a water bath (Ratek Instruments, Boronia, Victoria, Australia) and connected to a biogas collection gallery (Figure 3.2). The fermentation bottles (Wiltronics Research, Ballarat, Victoria, Australia) were sealed with a rubber bung and submerged in the water bath to maintain a temperature of 35.0 ± 0.1 °C. An S-shaped air lock and flexible plastic tubing were used to collect the biogas. The biogas collection gallery consisted of an array of inverted 1000 mL plastic measuring cylinders, which were initially filled with a NaOH solution (1 M). As biogas was introduced to the

cylinder, CO_2 and H_2S were sequestered by the NaOH solution, and the remaining CH_4 gas displaced the solution inside the cylinder. The volume of NaOH displaced by CH_4 gas was recorded every day.

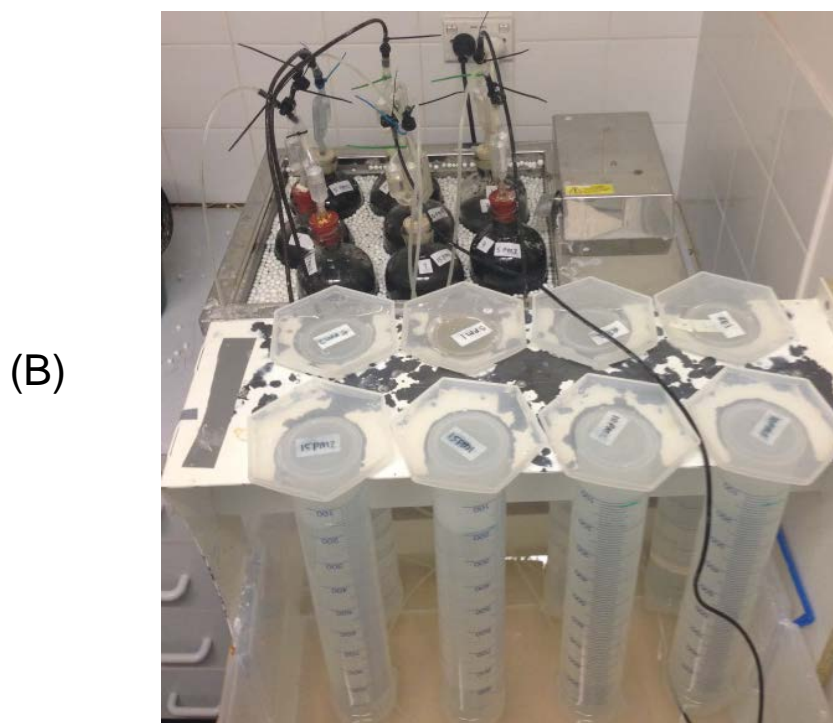
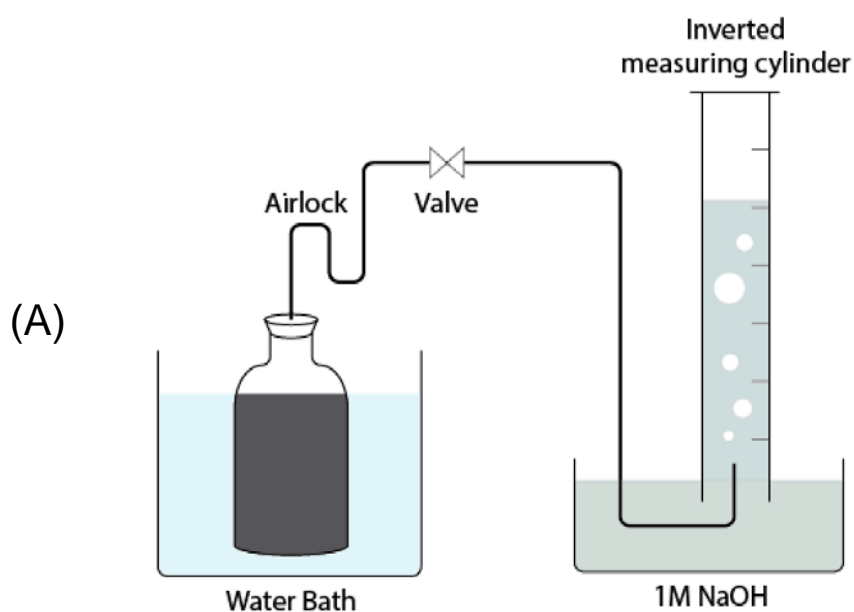


Figure 3.2. (A) Schematic diagram and (B) photo of the biochemical methane potential (BMP) set-up.

Equation 3.1 was used to calculate the amount of each draw solute to be added to the digested sludge, to simulate the reverse solute flux accumulation at 90% water recovery from pre-concentrated wastewater. The calculated amount of draw solute was firstly dissolved in 50 mL of DI water and then mixed with 700 mL of digested sludge. In the control BMP bottles, 50 mL of DI water was added to the same amount of digested sludge. The BMP bottle was purged with nitrogen gas, sealed, and connected to the gas collection gallery. All BMP experiments including the control were conducted in duplicate. The substrate in each bottle was characterised before and after the BMP experiment in terms of total solids (TS), volatile solids (VS), pH, alkalinity, total chemical oxygen demand (COD_T), and soluble chemical oxygen demand (COD_S).

3.2.6. Analytical methods

Temperature, pH, and electrical conductivity were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, Waltham, Massachusetts, USA). Conductivity measurements were used to determine the reverse draw solute flux of inorganic draw solutes. For neutral organic draw solutes, a Shimadzu TOC analyser (TOC-VCSH) was used to determine the reverse solute flux.

For digested sludge characterisation, TS, VS, and alkalinity were measured using standard methods [187]. COD was determined using a Hach DBR200 COD Reactor and Hatch DR/2000 spectrophotometer (program number 435 COD HR) following the US-EPA Standard Method 5220 D. For COD_S , the sludge supernatant was filtered through a 1 μ m filter paper and the filtrate was then analysed, whilst COD_T was measured by direct dilution of the homogenised sludge.

3.3. Results and discussion

3.3.1. Preliminary draw solution selection

Ten draw solutes were selected for experimental assessment to represent a range of inorganic and organic compounds. Sodium chloride was selected as a reference and magnesium sulphate was selected due to its reported low reverse solute flux through FO membrane (towards the bioreactor side), causing potentially minimal impact on anaerobic treatment [188]. Ionic organic draw solutions, namely sodium acetate, magnesium acetate, and sodium formate, were also selected due to their exhibition of a competitive water flux and potential benefits when combined with biological systems [156]. Ethylenediaminetetraacetic acid (EDTA) disodium salt has been previously studied by Hau,

et al. [189] for the concentration of wastewater sludge. Neutral organic draw solutes, including glucose, glycine, glycerol, and urea, were selected based on their moderate water flux and the anticipation for negligible effects on anaerobic treatment, independent of the magnitude of reverse solute flux [190]. Glycine has recently been investigated and found to be highly compatible with anaerobic digestion [180]. Each draw solute had previously shown potential for use as a FO draw solute for wastewater applications.

The molar concentration required to generate 30 bar of osmotic pressure varies significantly between the ten selected draw solutes. Overall, the required molar concentration varies from 0.3 M (EDTA disodium salt) to as high as 1.3 M (glycine).

Table 3.1. Molar concentration required to generate 30 bar of osmotic pressure and solute diffusion coefficients. Concentrations were calculated using OLI Stream Analyzer.

Draw solutes		Concentration (M)	Diffusion coefficient (m ² /s)	Reference
Inorganic	Sodium chloride	0.65	1.47×10^{-9}	[72]
	Magnesium sulfate	1.24	3.7×10^{-10}	[72]
Organic (ionic)	Sodium acetate	0.72	1.44×10^{-9}	[156]
	Magnesium acetate	0.84	1.14×10^{-9}	[156]
	Sodium formate	0.72	1.59×10^{-9}	[156]
	EDTA disodium salt	0.30	5.83×10^{-10}	[191]
Organic (covalent)	Glucose	1.13	6.7×10^{-10}	[192]
	Glycine	1.31	1.06×10^{-9}	[180]
	Glycerol	1.27	9.3×10^{-10}	[193]
	Urea	1.26	1.38×10^{-9}	[193]

3.3.2. Forward osmosis flux performance

3.3.2.1. Water and reverse solute flux

The draw solutions exhibited quite diverse flux performance despite being evaluated at the same osmotic pressure of 30 bar (Figure 3.3). Glycerol and urea could produce a moderate water flux (3.09 and 1.37 L/m²h, respectively) but the reverse solute fluxes were extremely high (15.2 and 106.3 g/m²h, respectively). These two draw solutions were eliminated from further analysis because the high reverse solute flux would result in excessive accumulation in pre-concentrated wastewater, as well as unsustainable FO operation. The remaining draw solutions exhibited a water flux in the range of 2.18–4.11 L/m²h. The observed variation in water flux at the same draw solution osmotic pressure could be attributed to the extent of ICP experienced by each solute [156, 188, 194]. ICP describes

the dilution of the draw solution in the membrane support layer which reduces the effective osmotic driving force and is affected by the draw solute kinetic characteristics including diffusivity, viscosity, and ion or molecule size [195].

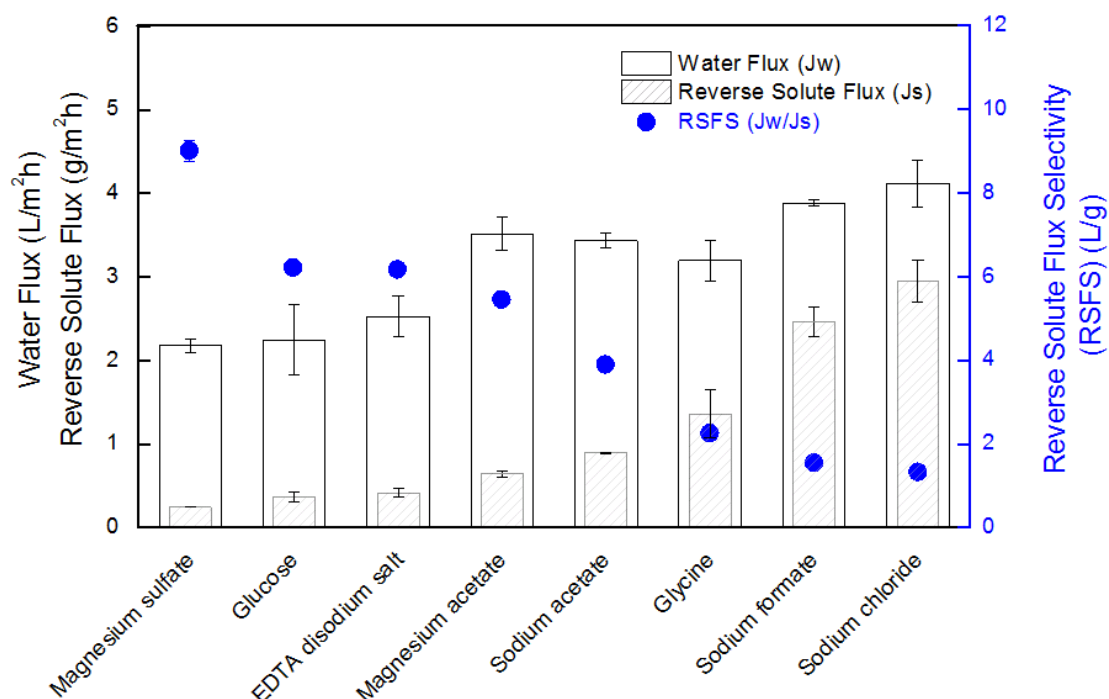


Figure 3.3. Average water flux, reverse solute flux and reverse solute flux selectivity (RSFS) at an osmotic pressure of 30 bar. Error bars represent the standard deviation of duplicate experiments.

Draw solute diffusivity strongly affected water flux and reverse solute flux (Figure 3.4). Water flux was linearly correlated to diffusion coefficient and clearly represented the extent of dilutive ICP for each solute. Solutes with low diffusivity experienced severe ICP and were more likely to display a low water flux. On the other hand, highly-mobile solutes could reduce the effects of ICP, and thus had a high water flux. This result is in good agreement with ICP theory, as within the relevant range, solutes with higher diffusion coefficients can produce a larger water flux at a constant bulk draw solution osmotic pressure [63, 195]. The results also show that reverse solute flux tended to increase exponentially for solutes with higher diffusion coefficients (Figure 3.4B). Thus, a trade-off exists between selecting highly diffusive draw solutes to maximise water flux and those which show low reverse solute flux.

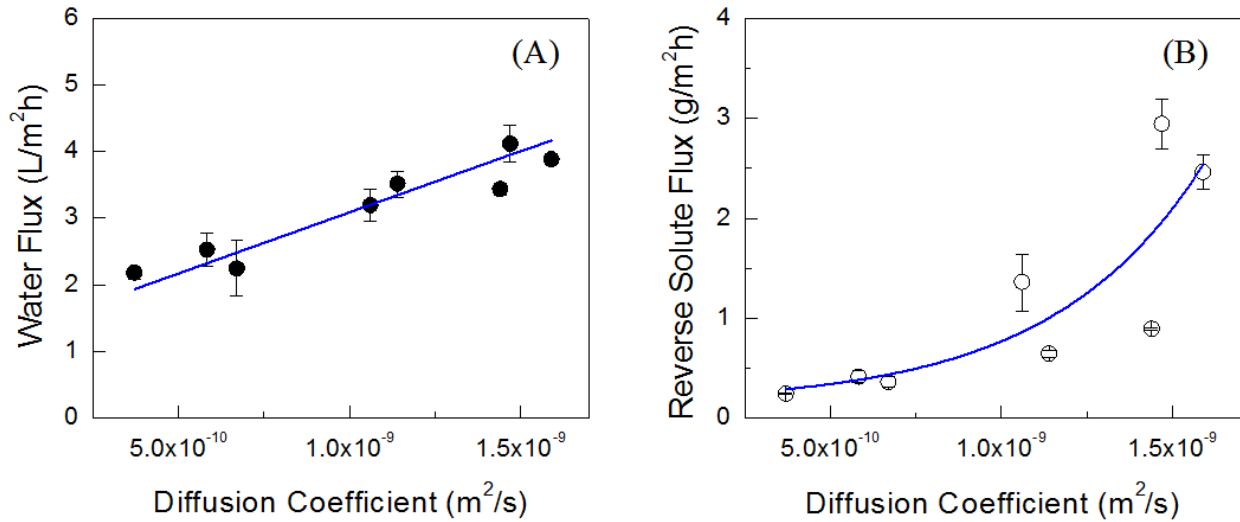


Figure 3.4: Relationship between diffusion coefficient and (A) water flux (linear regression $R^2 = 0.90$); (B) reverse solute flux (exponential regression $R^2 = 0.81$). Experiments were conducted at constant osmotic pressure (30 bar); error bars represent the standard deviation of duplicate experiments.

3.3.2.2. Reverse solute flux selectivity

In terms of draw solution replenishment cost and sustainable FO operation, a high RSFS is desirable. However, draw solutions that exhibited high RSFS generally had a correspondingly low water flux due to the effects of ICP (Figure 3.5). For example, magnesium sulphate had the highest RSFS of 9.01, but water flux was low ($2.18 \text{ L/m}^2\text{h}$). Interestingly, for most draw solutes investigated here, similar to the correlation between reverse solute flux and diffusion coefficient shown in Figure 3.4B, the water flux also decreased exponentially as the RSFS increased (Figure 3.5). Sodium acetate and magnesium acetate are the only two exceptions and their flux behaviour appeared to diverge from the trend of the other six draw solutes. Both solutes displayed a sufficiently high water flux ($>3 \text{ L/m}^2\text{h}$) but could also demonstrate suitably high RSFS values. One noticeable difference in behaviour between these two solutes was that magnesium acetate had a larger RSFS than that of sodium acetate due to a lower reverse solute flux. This could be attributed to the larger size of the magnesium cation, since both solutes share the same anion [188]. Furthermore, the use of ionic organic draw solutes appeared to benefit FO flux performance, particularly in the case of the acetate anion.

The expected concentration of draw solute within the pre-concentrated wastewater was estimated using Equation 3.1 (Table 3.2). Since the simulated concentration only depends on RSFS, solutes with a low RSFS result in larger concentrations, and alternatively, high RSFS ideally lowers the expected concentration. Nonetheless, inorganic salts are known to inhibit anaerobic treatment even at low concentrations [179].

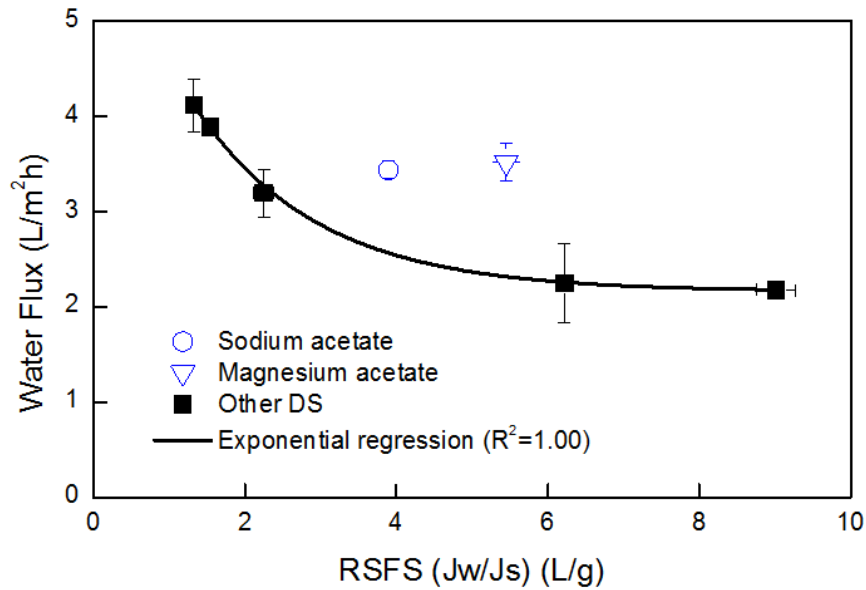


Figure 3.5. Variation of water flux with reverse solute flux selectivity (RSFS) to compare sodium acetate and magnesium acetate with other draw solutions (DS). Experiments were conducted at constant osmotic pressure (30 bar); error bars represent the standard deviation of duplicate experiments.

Table 3.2. Expected draw solute concentration (by reverse solute flux) in pre-concentrated wastewater assuming 90% FO system water recovery.

Draw solute	Concentration (g/L)
Sodium chloride	5.78
Sodium formate	5.45
Glycine	3.46
Sodium acetate	2.41
Magnesium acetate	1.65
EDTA disodium salt	1.52
Glucose	1.48
Magnesium sulfate	1.06

3.3.3. Effect of reverse draw solute flux on anaerobic treatment

Each draw solute had a noticeable impact on methane production over the 25 day observation period (Figure 3.6). The substrate characteristics before and after the BMP experiment are shown in Table 3.3. The organic draw solutes, namely, glycine, glucose, and the acetates displayed higher cumulative methane production compared to the control (no added draw solute), possibly because they are readily biodegradable. Glycine outperformed all other draw solutes. This might be attributed to its osmoprotectant properties, which can reduce osmotic stress caused by inhibitory constituents present in the digested sludge [196]. However, due to the low saline environment, enhanced methane production was most likely a result of the relatively high concentration of glycine dosed (3.46 g/L). Similarly, even at a lower concentration (1.48 g/L), glucose promoted methane production by providing additional organic substrate. Sodium acetate presented a similar methane production to glucose, and only slightly higher than magnesium acetate. The presence of the sodium or magnesium cation appeared not to affect acetate conversion; however sodium acetate (2.41 g/L) was dosed at a higher concentration than magnesium acetate (1.65 g/L). The results suggest that these draw solutes have a positive effect on methane production and would be suitable when integrating FO with anaerobic treatment.

EDTA disodium salt and sodium formate exhibited a similar cumulative methane production to the control. EDTA disodium salt was expected to enhance methane production by increasing the bioavailability of essential elements [197]; however, no additional methane production was observed, possibly because the concentration used in this study was significantly higher than that found to be beneficial by Vintiloiu, et al. [197]. The methane production of sodium formate was stable, but occurred at a slower rate compared to that of the control. This could be attributed to the high sodium concentration of 1.8 g Na/L, particularly when compared with sodium acetate which contained only 0.7 g Na/L. Additionally, the COD contribution of acetate (1.07 g COD/g) is much larger than formate (0.34 g COD/g) and would have promoted a faster and more consistent rate of methane production [198].

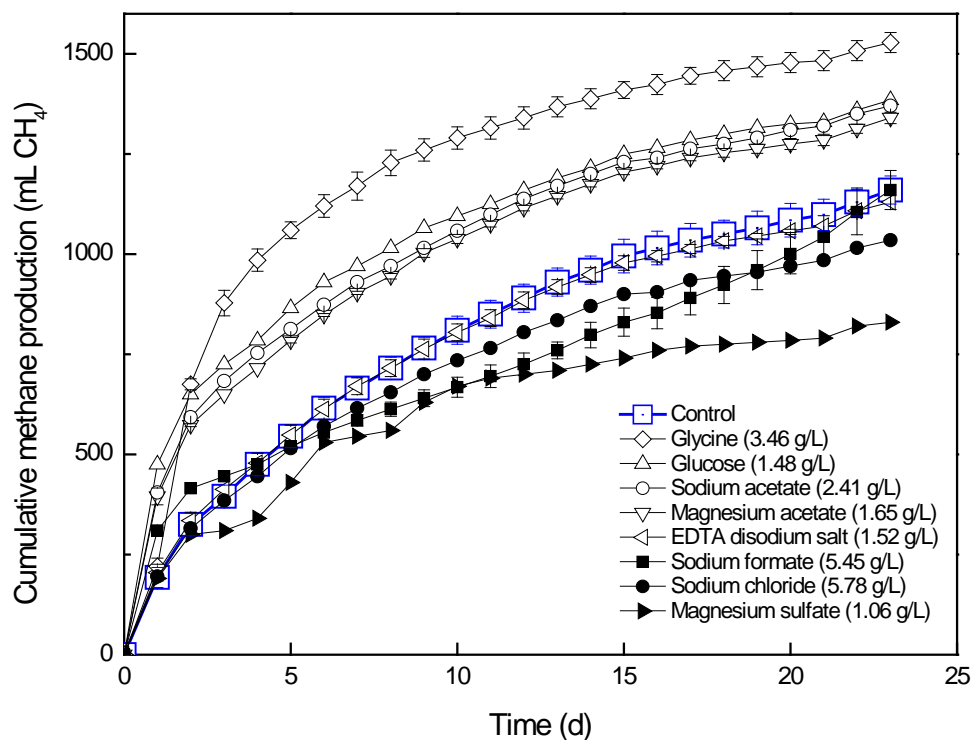


Figure 3.6. Cumulative methane production of digested sludge with dosed draw solute at concentrations corresponding to FO RSFS and 90% system recovery; error bars represent the standard deviation of duplicate experiments.

Table 3.3. Substrate characterisation for BMP experiments (average concentration \pm standard deviation from duplicate measurements).

Draw solute	TS (% w/w)		VS (% w/w)		pH		Alkalinity (mg CaCO ₃ /L)		COD _T (g/L)		COD _S (g/L)	
	T ₀	T _F	T ₀	T _F	T ₀	T _F	T ₀	T _F	T ₀	T _F	T ₀	T _F
Reference	2.5	1.4	1.7	0.9	7.20	7.13	2298	3120	22.9	9.4	1.38	0.82
Magnesium sulfate	2.6	1.7	1.4	1.1	7.17	7.10	2346	3120	26.0	15.3	1.26	0.50
Glucose	2.7	1.8	1.8	1.2	7.18	7.08	2032	3096	23.3	16.7	2.72	0.39
EDTA disodium salt	2.6	1.8	1.0	1.2	7.08	7.13	2564	3411	25.2	13.9	2.34	1.05
Magnesium acetate	2.5	1.4	1.6	0.9	7.12	7.07	2588	3604	24.0	9.2	1.85	0.46
Sodium acetate	2.8	1.7	1.9	1.1	7.17	7.09	2879	3943	23.0	11.1	2.30	0.52
Glycine	2.8	1.4	1.0	0.9	7.13	7.32	2322	5273	27.4	12.5	3.24	1.46
Sodium formate	3.0	2.1	1.8	1.1	7.12	7.66	3628	6918	24.8	9.3	2.24	2.27
Sodium chloride	3.1	2.4	1.0	1.2	7.07	7.08	2250	3000	28.2	12.8	1.41	1.16

Inorganic draw solutes had a negative effect on methane production over the observation period. Sodium chloride had only slight negative effects on methane production, most likely caused by the dehydration of bacterial cells due to osmotic pressure [179]. This inhibition observed at 2.3 g Na/L is slightly lower than the 3 g Na/L reported to be toxic to methanogenic bacteria [159]. Therefore, the presence of sodium chloride in pre-concentrated wastewater by reverse draw solute flux is expected to have a small but discernible effect on anaerobic treatment. Inhibition caused by magnesium sulphate at 1.06 g/L was found to be more prominent than sodium chloride. The low methane yield observed for magnesium sulphate was likely due to the competition for substrate between sulphate reducing and methane producing bacteria. Inhibitory concentrations for methanogens have been reported to be as low as 1.4 g SO_4^{2-} /L [199] which is in good agreement with the results of this study. Despite other advantages associated with the use of inorganic salts, the use of these draw solutes is not recommended when integrating FO with anaerobic treatment, with current FO membranes.

Independent of the draw solution and reverse solute flux, elevated salt concentrations would be expected due to the concentration of the natural salinity of wastewater during the FO process. In the case of inorganic draw solutions, further inhibition of methane production and inefficiencies in the anaerobic digestion process could be expected. For the organic draw solutions demonstrated to be beneficial for anaerobic treatment, the salinity of the pre-concentrated wastewater would not be significantly exacerbated by reverse solute flux. Furthermore, significantly higher COD concentrations would be achieved during wastewater pre-concentration as a result of the contribution of reverse solute flux, allowing the opportunity to operate at a lower concentration factor.

3.3.4. Draw solute suitability for anaerobic treatment

Sodium acetate and magnesium acetate were two draw solutions that ranked high in terms of FO flux performance. Both exhibited a slightly lower water flux when compared with sodium chloride; however, their reverse solute flux was significantly lower. In FO wastewater applications, a low reverse solute flux is crucial for maintaining flux sustainability, lowering replenishment costs, and reducing salinity build-up. In terms of BMP, glycine demonstrated significant potential for anaerobic treatment. Glucose, sodium acetate, and magnesium acetate were also suitable, as their presence in pre-concentrated wastewater could enhance methane production. Overall, sodium acetate ranked highly in terms of FO flux performance

and suitability for anaerobic treatment, as well as providing cost advantages over magnesium acetate in terms of specific cost [156].

Ionic organic draw solutes were found to be the most suitable and therefore further implications exist. Detailed investigations into flux sustainability, the potential aggravation of organic fouling and compatibility with reconcentration processes are required. As previously mentioned, the retention and accumulation of feed salinity also require further examination, in terms of reducing the osmotic driving force and also the compatibility with anaerobic treatment.

3.4. Conclusions

This study assessed draw solution flux performance and the impact of reverse solute flux on the anaerobic treatment of FO pre-concentrated wastewater. The results show that ionic organic draw solutes such as sodium acetate are most suitable for this application, due to the acceptable flux performance and benefits towards methane production. The effects of inorganic salts on anaerobic treatment were also demonstrated. The reverse solute flux of sodium chloride only exerted a small but discernible inhibitory effect on methane production. The BMP test could be a reliable screening tool for assessing draw solution compatibility with anaerobic digestion.

CHAPTER 4: Factors governing the pre-concentration of wastewater using forward osmosis for subsequent resource recovery

Corresponding publication:

A.J. Ansari, F.I. Hai, W. Guo, H.H. Ngo, W.E. Price and L.D. Nghiem, Factors governing the pre-concentration of wastewater using forward osmosis for subsequent resource recovery, Science of the Total Environment, 566-567 (2016), 559-566.

4.1. Introduction

The shift from aerobic to anaerobic biological treatment processes is a necessary step to achieve energy efficient wastewater treatment and to facilitate resource recovery practices [14, 32, 111]. Anaerobic treatment has two major advantages over aerobic treatment, namely energy recovery via methane production and reduced energy input, since aeration is not required [24]. Furthermore, anaerobic effluent represents a practical platform for nutrient recovery [152, 200].

In general, municipal wastewater is not suitable for direct anaerobic treatment. Indeed, given the low organic matter content of municipal wastewater (indicated by a chemical oxygen demand (COD) of usually < 500 mg/L), the thermal energy and physical footprint required for anaerobic treatment can be excessive. Importantly, anaerobic treatment requires a feed solution in excess of 1000 mg COD/L to ensure system stability and process efficiency [201]. An innovative approach to overcome the challenges associated with the anaerobic treatment of municipal wastewater involves the initial pre-concentration of organic matter prior to feeding the digester.

The net energy recovery of anaerobic systems is theoretically proportional to the COD of the feed solution. Thus, pre-concentrating the organic matter in wastewater can significantly benefit the economics of anaerobic treatment processes. An ideal pre-concentration process would essentially separate water and non-aqueous components, to produce high quality water for reuse and a concentrate stream suitable for anaerobic treatment. Previously suggested methods include dynamic sand filtration, dissolved air flotation, and bio-flocculation [14, 32]. However, these systems have limited organics retention capability and effluent from these

processes still requires membrane filtration to produce water suitable for reuse. High rejection membrane processes such as nanofiltration (NF) and reverse osmosis (RO) can pre-concentrate the organic content of wastewater. Yet, they are not suitable for direct wastewater treatment and require extensive pre-treatment to control membrane fouling. Thus, the application of advanced separation technologies which can handle complex wastewater and achieve low energy treatment will be pivotal to developing sustainable wastewater treatment practices.

Forward osmosis (FO) is a membrane process with significant advantages when applied to wastewater treatment for fresh water production and resource recovery [39, 61]. Unlike pressure driven membrane processes, the driving force of water permeation for FO is the osmotic pressure gradient between the feed solution (wastewater) and the draw solution (e.g. NaCl) [59]. FO can directly pre-concentrate wastewater without significant external energy input [59, 61, 121]. Furthermore, the nature of the driving force means that the process has a low fouling propensity and fouling can be highly reversible [80, 103, 202]. Therefore, treatment of complex matrices such as wastewater by FO is feasible and key constituents including organic matter and nutrients can be retained in the concentrate. Fresh water can also be recovered from the draw solution by applying an additional desalination process such as NF [126], RO [106, 107], or membrane distillation (MD) [97, 129]. In particular, as a thermally driven desalination processes, MD presents a unique opportunity, as the required thermal energy could be supplied by solar thermal energy or from biogas co-generation produced from the subsequent anaerobic digestion of pre-concentrated wastewater [203].

FO is recognised as a promising approach to pre-concentrate wastewater prior to anaerobic treatment [65, 111, 180], however this approach is yet to be fully explored. Recent studies have focused almost exclusively on the integration of FO and anaerobic treatment to form an anaerobic osmotic membrane bioreactor (An-OMBRs) [54, 56, 57] or to filter anaerobic effluent [165, 166, 204]. To date, very few studies have investigated the use of FO for direct treatment of municipal wastewater [65, 66, 97]. The FO wastewater pre-concentration concept allows for the simultaneous extraction of clean water for beneficial reuse whilst pre-concentrating wastewater to a higher strength suitable for anaerobic treatment. In this approach, a higher degree of control and accessibility exists for the FO component as it is not confined within a bioreactor, as is the case for An-OMBRs. In their recent work, Zhang, et al. [65] demonstrated the FO wastewater pre-concentration process, however due to the limitations of their experimental set-up, could only demonstrate a COD

concentration factor of approximately three. Wang, et al. [66] presented the treatment performance of a spiral wound FO module to concentrate wastewater. Nevertheless, issues of salinity accumulation and anaerobic treatment integration were not addressed by Wang, et al. [66].

Although there is growing interest in the application of FO for wastewater pre-concentration and subsequent energy/resource recovery, the assessment of key performance factors has not been systematically investigated to date. Several challenges must be addressed for the implementation of the proposed FO wastewater pre-concentration process. Firstly, salinity accumulation is a major problem for high retention membrane systems such as FO, and particularly when combined with a sensitive biological process [49, 109, 205]. Secondly, membrane fouling remains a prominent challenge for the sustained wastewater filtration of such complex wastewater solutions [65, 97, 112, 117]. These challenges and the potential solutions explored in this chapter are graphically displayed in Figure 4.1.

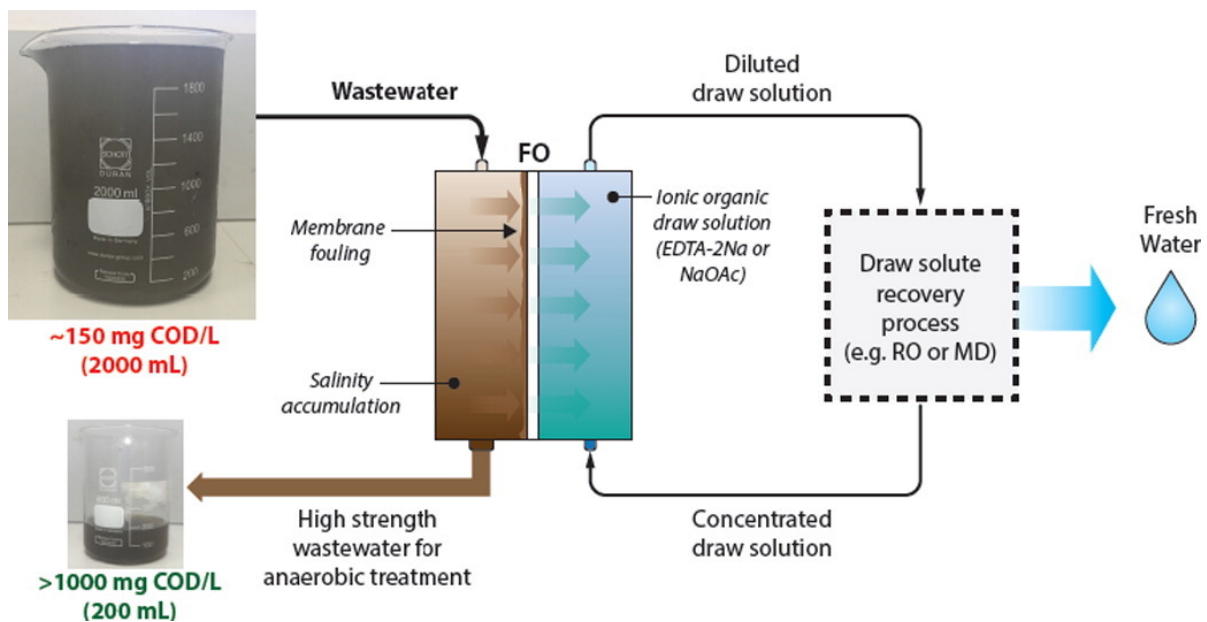


Figure 4.1. Graphical representation of the challenges and potential solutions relating to wastewater pre-concentration using the FO process.

This chapter aims to elucidate the key factors governing FO membrane performance during wastewater pre-concentration. The effectiveness of FO at pre-concentrating wastewater was examined by evaluating the ability of the FO membrane to retain COD at different water recoveries. Next, we evaluated the use of ionic organic draw solutes to mitigate salinity build-up. The effect of the selected draw solution on the produced clean

water flux, COD, and pH of the concentrated wastewater was also investigated. Lastly, the extent of membrane fouling was assessed and hydrodynamic conditions were optimised. Both batch and continuous flow experiments were conducted to observe FO membrane fouling behaviour with real wastewater under intense pre-concentration conditions. Overall, this study proposes the importance of draw solution selection and optimised hydrodynamic conditions for the application of FO for wastewater pre-concentration.

4.2. Materials and methods

4.2.1. Materials and chemicals

Cellulose triacetate (CTA) membrane with a non-woven support was used in this study and was acquired from Hydration Technologies Innovation (Albany, Oregon, USA). The overall thickness of this non-woven CTA membrane is 144 μm . The average pore size is expected to be similar to that of a CTA membrane with embedded support which has been reported to be 0.37 μm by Xie, et al. [206]. Experiments were conducted with analytical grade draw solutes, at a constant osmotic pressure of 60 bar. The concentration of each draw solution at this pressure was calculated using OLI Stream Analyzer (OLI Systems, Inc., Morris Plains, New Jersey, USA). Sodium chloride, sodium acetate, and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were used as draw solutions and the concentrations corresponding to 60 bar osmotic pressure were 1.27, 1.49, and 0.61 M, respectively.

Primary effluent (i.e. wastewater after primary sedimentation) was obtained from Wollongong Wastewater Treatment Plant (Wollongong, Australia). All batch experiments were conducted using both low and moderate strength wastewater, to represent the variability of municipal wastewater influent quality. Moderate strength wastewater was obtained during a dry weather period. Low strength wastewater was obtained immediately after a wet weather period.

4.2.2. Forward osmosis system

A lab-scale, cross-flow FO membrane system was used. The membrane cell had two symmetric flow channels both with length, width, and height of 250, 50, and 2 mm, respectively, resulting in an effective membrane area of 125 cm^2 . The feed and draw solutions were continuously circulated through each flow channel by two variable speed gear pumps (Micropump, Vancouver, Washington, USA). The flow rate was regulated by two rotameters and was adjusted to achieve the desired cross-flow velocity. The majority of

experiments were operated with 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s). A spacer was placed on the draw solution side of the membrane to improve mixing.

The draw solution reservoir was positioned on a digital balance (Mettler-Toledo Inc., Hightstown, New Jersey, USA) and weight changes were recorded to calculate permeate water flux. A reservoir containing a highly concentrated stock solution (5 M) was also placed on the digital balance and was automatically dosed into the draw solution to maintain a constant osmotic pressure during experiments. The conductivity of the draw solution was monitored using a conductivity probe (Cole-Parmer, Vernon Hills, Illinois, USA), and was connected to a controller and a peristaltic pump to automatically regulate the draw solution concentration (control accuracy of ± 0.1 mS/cm).

4.2.3. Experimental protocol

All experiments were conducted in FO mode (i.e. active layer facing the feed solution). Analytical grade solutes were dissolved in DI water at concentrations corresponding to an osmotic pressure of 60 bar. Water flux was measured according to the standard procedure previously described by Cath, et al. [186]. Water recovery was used to represent the FO water extraction rate and was calculated based on the ratio of the cumulative permeate volume and the initial feed solution volume.

For batch experiments, the FO system was used to process primary effluent until a water recovery of 90% had been achieved. The initial volume of primary effluent (i.e. feed solution) was 2 L, and the solution was continuously filtered until 90% of the feed solution had permeated through the membrane (i.e. permeate volume of 1.8 L). Water flux was continuously monitored. The conductivity, pH, and temperature of each solution were also regularly measured. A 10 mL sample was withdrawn from the feed solution at specific time intervals for COD analysis as a measure of the strength of the wastewater or concentrated solution. All batch experiments were conducted in duplicate.

A continuous flow experiment was also conducted whereby 5 L of primary effluent was firstly processed to achieve 90% water recovery, leaving 0.5 L of pre-concentrated solution. At this point, the membrane was flushed with DI water to remove the fouling layer. The system was then continuously operated using a feeding and concentrate withdrawal regime (maintaining 90% water recovery). Two Masterflex peristaltic pumps (Cole-Parmer, Vernon Hills, Illinois, USA) were used to supply fresh primary effluent into the feed solution reservoir and to withdraw concentrate. The experiment was terminated approximately 90 h

after membrane flushing, when the water flux had reduced to half of the initial water flux. Sodium chloride was used as the draw solution for all continuous flow experiments.

Detailed reverse solute flux experiments were conducted to elucidate solute transport behaviours of the ionic organic draw solutes. The feed solution consisted of 3 L of DI water and the respective draw solution had a constant osmotic pressure of 60 bar. The conductivity, pH, and temperature of solutions were measured hourly. The reverse draw solute flux of each draw solution was measured by monitoring the changes of conductivity in the feed solution over time. A 20 mL sample was also withdrawn from the DI water feed solution reservoir for subsequent analysis of sodium and total organic carbon (TOC) to determine the reverse solute flux of sodium, and acetate and EDTA, respectively.

4.2.4. Analytical methods

Key water quality parameters of the primary effluent were measured according to standard methods. COD was measured using a Hach DRB200 COD Reactor and Hach DR3900 spectrophotometer (program number 435 COD HR) following the US-EPA Standard Method 5220. Adequate dilutions and adjustments were made to minimise chloride interference during sample measurements. A Shimadzu analyzer (TOC- V_{CSH}) was used to determine TOC concentration. An inductively coupled plasma-optical emission spectroscopy (ICP-OES) system (ICP-OES 710, Agilent, Australia) was used to determine the sodium ion concentration in the samples. Temperature, pH, and electrical conductivity were measured using an Orion 4-Star pH/conductivity meter (Thermo Scientific, Waltham, MA).

4.3. Results and discussion

4.3.1. Forward osmosis pre-concentration of organic matter in wastewater

Low strength wastewater can be pre-concentrated by FO up to the range suitable for anaerobic digestion (i.e. approximately 1000 mg COD/L). In this study, both low strength (137 ± 8 mg COD/L), and moderate strength wastewater (356 ± 13 mg COD/L) were pre-concentrated until 90% water recovery was achieved (Figure 4.2A). The FO process predominantly extracted clean water, therefore enriching the concentration of organic matter in the feed solution. Results show that the FO process consistently pre-concentrated COD up to approximately eight-fold, independent of the initial wastewater COD. The low and moderate strength wastewater COD concentrations were increased up to 982 ± 61 and 2893 ± 70 mg/L, respectively. These results demonstrate the suitability of FO for pre-concentrating wastewater, and its robustness for treating wastewater with variable influent

quality. Furthermore, pre-concentrating wastewater with FO produces a reduced solution volume (i.e. ten times reduction at 90% water recovery) that is rich in organics and is arguably more amenable to anaerobic digestion compared to directly digesting raw wastewater.

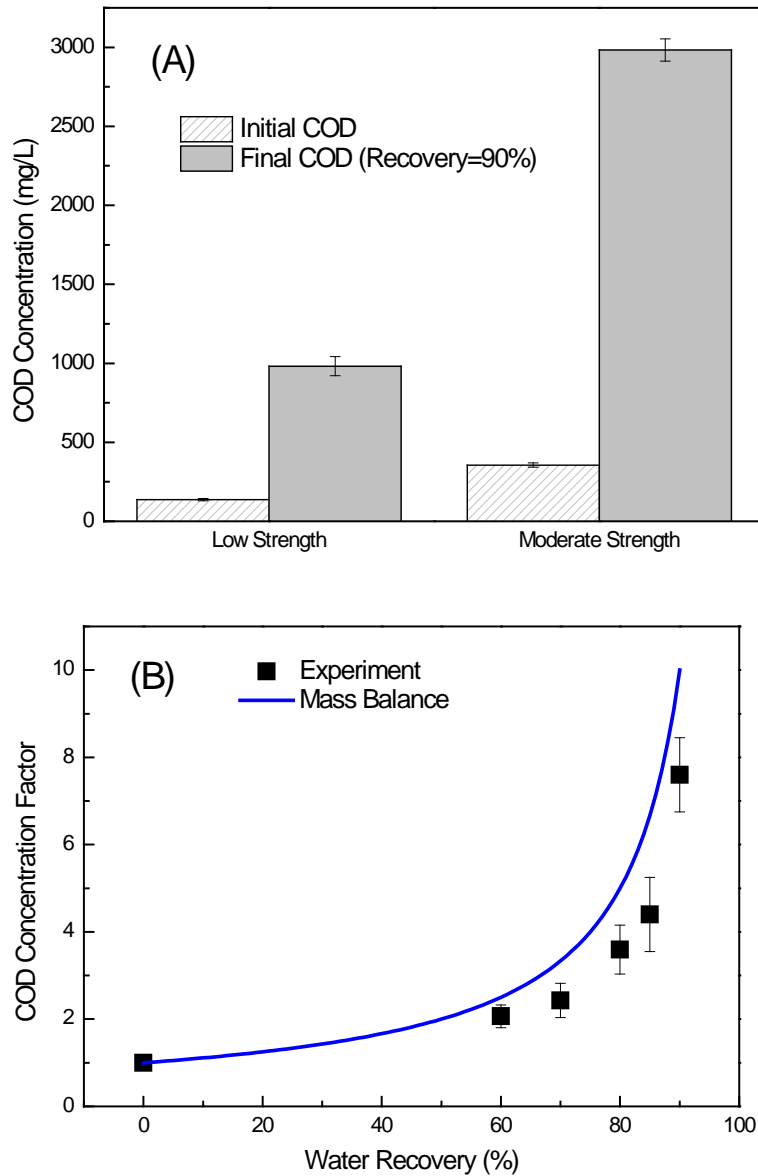


Figure 4.2. (A) Initial and final (i.e. at water recovery of 90%) COD concentrations for low and moderate strength wastewater. Error bars represent the standard deviation of triplicate COD sample measurements. (B) Variation of experimental and calculated wastewater COD concentration factor during FO pre-concentration. Error bars represent the standard deviation of triplicate COD sample measurements from duplicate experiments. The initial wastewater COD for low and moderate strength wastewater were 137 ± 8 mg/L, and 356 ± 13 mg/L, respectively. Mass balance assumes 100% COD retention in feed solution. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar, NaCl draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s).

The concentration of COD in wastewater increased proportionally with the FO system water recovery (Figure 4.2B). The FO membrane effectively retained a large proportion of organic matter in the feed solution, shown by the comparability of the experimental COD concentration with the calculated mass balance (i.e. assuming 100% COD retention in the feed solution). The experimental results were only slightly lower than values obtained from mass balance calculation and this observation can possibly be explained by the accumulation of solid organics within the membrane cell. In other words, a portion of the bulk pre-concentrated wastewater COD gradually formed a cake layer on the membrane surface. Therefore, the measured feed solution COD concentration was lower than expected, particularly at high water recoveries where solids content was high. To a lesser degree, the observed COD pre-concentration behaviour may also relate to the incomplete rejection of COD by the FO membrane (i.e. 99% rejection) [117]. Theoretically, the COD concentration factor could be further maximised by increasing water recovery, or when higher strength wastewater is used as the feed solution (i.e. > 500 mg COD/L), yet this would further exacerbate the issues of salinity accumulation (Section 4.3.2.1) and membrane fouling (Section 4.3.3). The eight-fold concentration of COD achieved in this study is substantially higher than previous studies (i.e. three-fold COD concentration) [65] and is attributed to the longer process filtration time and potentially the lower initial COD of the wastewater.

The enhanced organic content of FO concentrated wastewater can enable this solution to be fed into an anaerobic digester, and is arguably more effective when compared to direct anaerobic digestion of dilute wastewater. The net energy recovery from an anaerobic digester is theoretically proportional to the feed COD concentration, and therefore the FO system water recovery [111]. Thus, the increased COD concentration of FO pre-concentrated wastewater would increase energy recovery per unit volume of digestate. Furthermore, since 90% of the initial water content has been extracted by the FO process for further treatment, the volume of feed that requires heating to optimum mesophilic conditions (i.e. 35 °C) during anaerobic treatment is lowered ten-fold (when compared with raw wastewater). In addition, when the FO process is combined with other desalination processes, high quality water can be reclaimed for reuse [60]. Overall, FO presents a direct and robust approach to wastewater treatment, by focusing on pre-concentrating organic matter to facilitate subsequent anaerobic digestion for energy recovery.

4.3.2. Ionic organic draw solutes for wastewater pre-concentration

4.3.2.1. Salinity accumulation

Salinity accumulation is a major hindrance for high retention membrane systems such as FO, particularly when coupled with a biological process [49]. Intensive pre-concentration of wastewater by FO leads to the accumulation of salinity in the feed solution via two mechanisms. Firstly, the natural salinity of wastewater is retained by the FO membrane, and therefore the salt concentration increases proportionally to the system water recovery. Secondly, salt leaks from the draw solution into the feed solution (i.e. reverse draw solute flux) and can also significantly contribute to salinity accumulation [59]. Salinity accumulation in FO systems can have detrimental effects on water flux, as the osmotic pressure of the feed solution is increased, thereby reducing the effective osmotic driving force. More importantly for this application, high salt content within the pre-concentrated wastewater could potentially have adverse effects on subsequent anaerobic treatment processes.

A promising approach to mitigate salinity build-up in FO pre-concentrated wastewater involves the use of ionic organic draw solutes. When sodium chloride was used as the draw solution, the conductivity of wastewater significantly increased as water recovery increased (Figure 4.3A). On the other hand, ionic organic draw solutes such as sodium acetate and EDTA-2Na presented a significantly lower conductivity compared to sodium chloride, demonstrating effective mitigation of salinity accumulation. A similar result was expected by Bowden, et al. [156] when using ionic organic draw solutes in an aerobic osmotic membrane bioreactor. Because each experiment pre-concentrated wastewater to 90% water recovery, the main contributor to the variance in salinity was the reverse draw solute flux. As shown in Figure 4.3B, the extent of salt accumulation was inversely related to the magnitude of reverse solute flux selectivity (RSFS) for each draw solution. Both sodium acetate and EDTA-2Na exhibited a larger RSFS compared to sodium chloride, indicating that a smaller amount of solute diffused through the membrane for a constant permeate volume. Thus, adopting ionic organic draw solutions could achieve a pre-concentrated solution with a lower salinity, without compromising the achievable organic content in pre-concentrated wastewater.

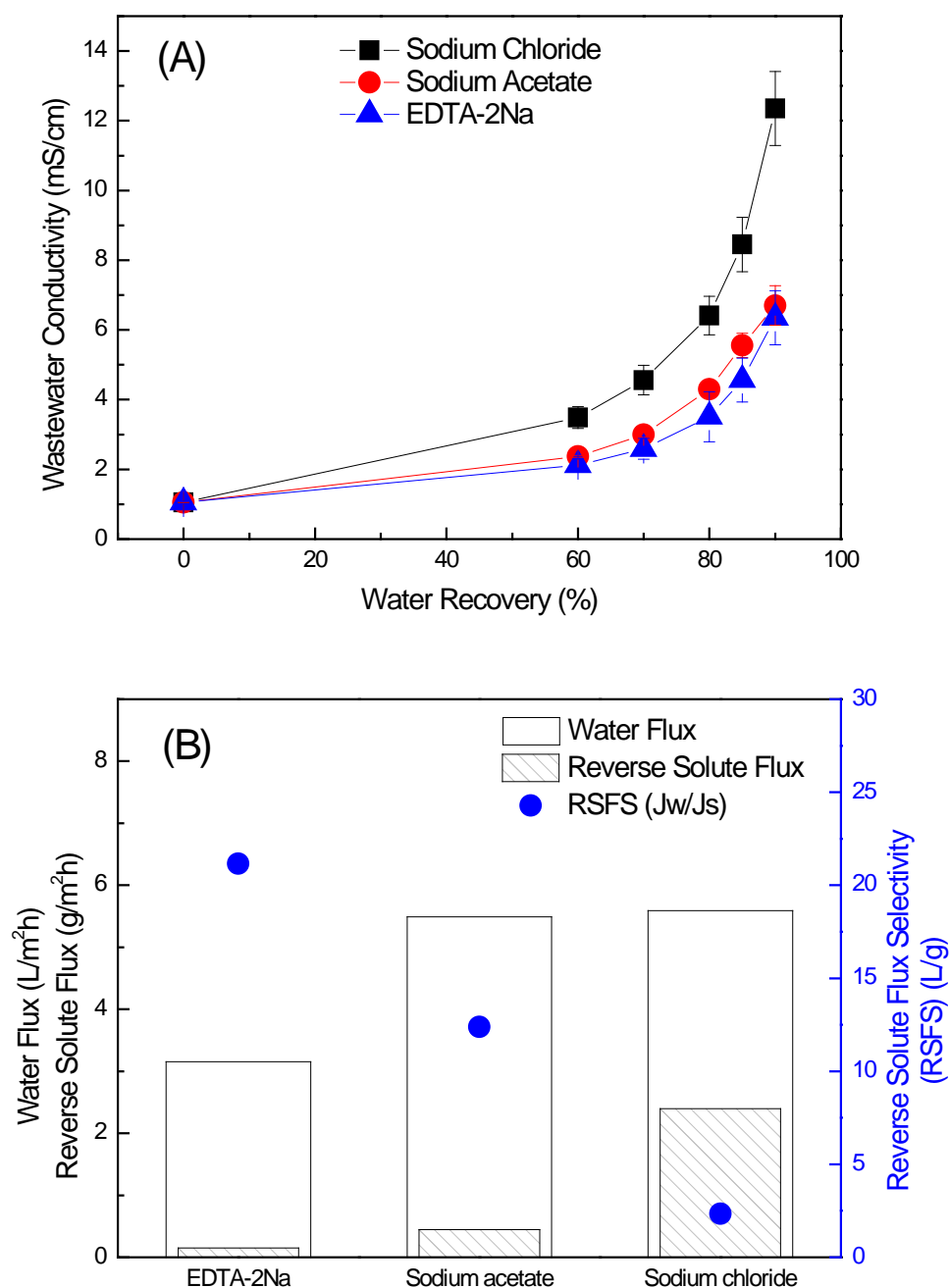


Figure 4.3. (A) Variation of wastewater conductivity during wastewater pre-concentration for sodium chloride, sodium acetate, and EDTA-2Na. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s). The initial wastewater conductivity was 1.05 ± 0.02 mS/cm. (B) Water flux, reverse solute flux, and reverse solute flux selectivity (RSFS) of sodium chloride, sodium acetate, and EDTA-2Na. Experimental conditions: as above, with DI water feed solution (4 L). Error bars represent the standard deviation of measurements from duplicate experiments.

The lower reverse solute flux behaviour of sodium acetate and EDTA-2Na can be explained by the mobility of the draw solute molecule. Both draw solutes have a lower diffusivity compared to sodium chloride, as acetate and EDTA ions are significantly larger than chloride as reported in Chapter 3. Thus, solute diffusion from the draw solution to the feed solution is restricted. This has implications for the attainable water flux for each draw solution (Section 4.3.2.3). Binary ion analysis for sodium acetate showed a similar performance to sodium chloride, whereby both the cation and anion diffused into the feed solution at a similar rate (Figure 4.4A). In contrast, binary ion analysis for EDTA-2Na revealed the potential decoupling of sodium and EDTA diffusion rates (Figure 4.4B). In other words, sodium tended to diffuse through the FO membrane at a faster rate than EDTA. This is likely due to the large size and high negative charge of EDTA, minimising EDTA diffusion through the membrane [189]. Nonetheless, despite the identified decoupling of the EDTA-2Na draw solute, compared to sodium chloride and sodium acetate, the reverse salt flux with respect to only sodium was still insignificant. The combination of EDTA with solutes other than sodium has also shown potential to minimise reverse solute flux and would greatly benefit the FO pre-concentration process [126].

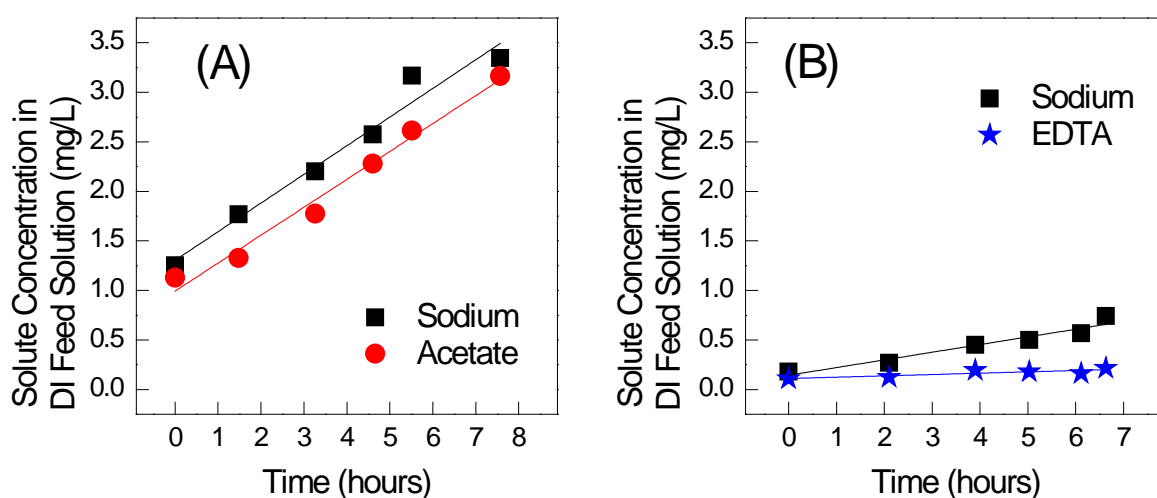


Figure 4.4. Ionic organic draw solution binary ion diffusion analysis with linear regressions. (A) Sodium acetate and (B) EDTA-2Na. Experimental conditions: As in Figure 4.3B.

4.3.2.2. COD content of pre-concentrated wastewater

In addition to mitigating salinity build-up, ionic organic draw solutes enhance COD when pre-concentrating low strength wastewater. At 90% water recovery, both sodium acetate and EDTA-2Na displayed higher COD concentrations compared to sodium chloride (Figure 4.5A). This may be due to the reverse solute flux of the ionic organic draw solutes, enhancing the COD concentration of the low strength wastewater. Although reverse solute flux is generally viewed as a hindrance for the FO process, in the case of ionic organic draw solutes, the mechanism could be beneficial for subsequent anaerobic treatment. For example, unlike sodium chloride which inhibits methane production during anaerobic treatment, the presence of sodium acetate or EDTA-2Na in pre-concentrated wastewater can benefit methane production (Chapter 3). By adopting ionic organic draw solutes when treating low strength wastewater, opportunities exist to operate at a favourably lower water recovery, whilst attaining the desired COD range and allowable salinity level. On the other hand, for moderate strength wastewater, the contribution of reverse solute flux to COD concentration was negligible (Figure 4.5B). The higher initial COD of the wastewater may have masked the contribution by reverse solute flux, and was possibly the reason why all three draw solutes displayed similar COD concentration performance.

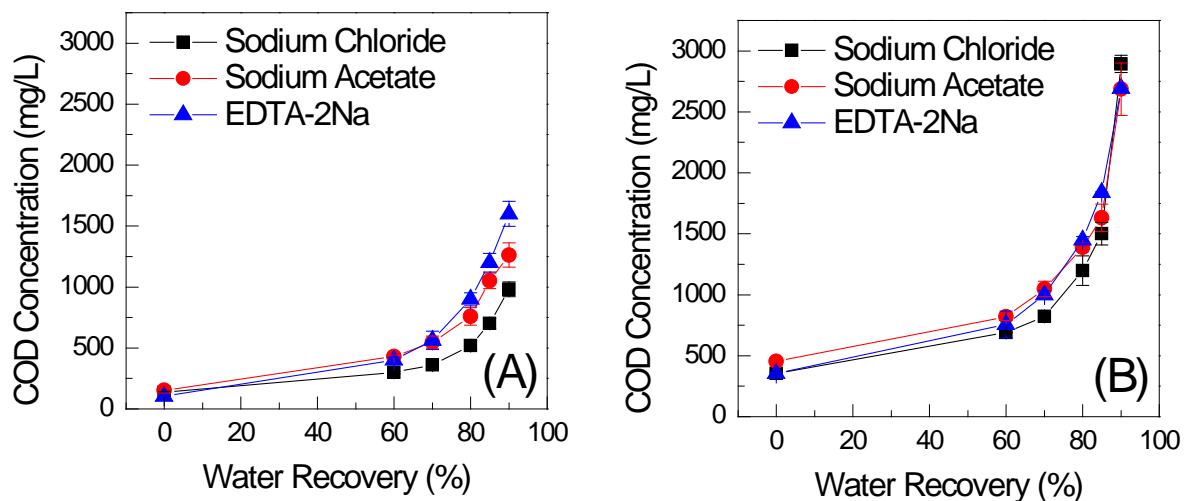


Figure 4.5. Variation of COD concentration during wastewater pre-concentration for (A) low strength and (B) moderate strength wastewater. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s). Error bars represent the standard deviation of triplicate COD measurements.

4.3.2.3. Effect of draw solute on water flux decline

During the batch wastewater pre-concentration experiments, the choice of draw solute did not significantly affect water flux decline even at high water recovery values (Figure 4.6). This suggests that both membrane fouling and salinity accumulation did not significantly contribute to water flux decline under these conditions (i.e. small processing volume and 90% water recovery cycle). As discussed in Section 4.3.3, continuous operation did result in more severe membrane fouling. For these batch experiments, the osmotic pressure of the pre-concentrated wastewater was significantly lower than the draw solution throughout the experiment. Flux decline was likely caused by the sparse accumulation of foulants on the membrane surface, as the implemented hydrodynamic conditions (i.e. increased cross-flow velocity) prevented excessive build-up of foulant materials.

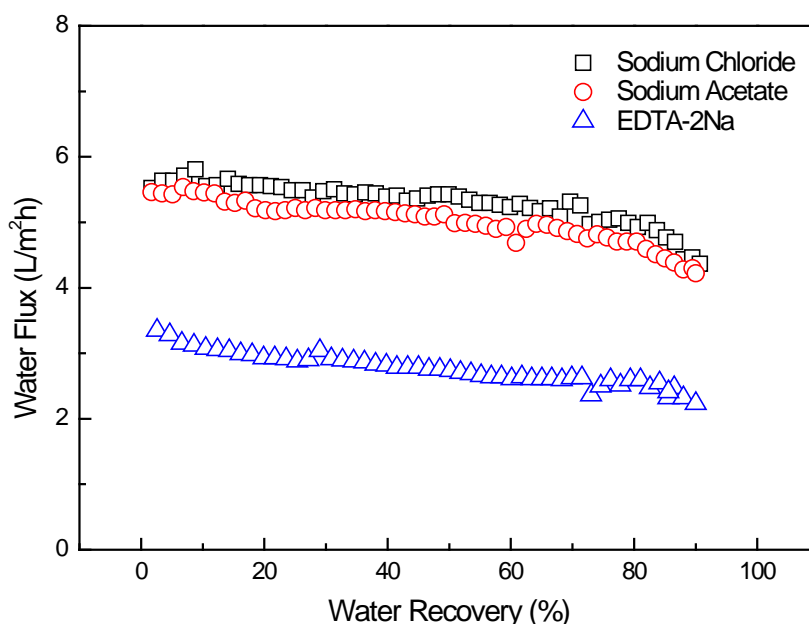


Figure 4.6. Water flux decline during batch wastewater pre-concentration. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s).

Although the draw solution did not affect water flux decline, the initial water flux was significantly governed by the draw solution. Sodium chloride and sodium acetate gave similar initial water fluxes (5.5 and 5.4 L/m²h, respectively) at the same osmotic pressure (i.e. 60 bar), whilst the initial water flux of EDTA-2Na was significantly lower (3.3 L/m²h). EDTA-2Na exhibited the lowest water flux, owing to the negative effects of internal concentration polarisation [195]. This has limitations regarding the scale-up of FO systems

using EDTA based draw solutions, since a large membrane area would be required. Nonetheless, since FO is an osmotically driven process, other operational costs would not be significantly impacted.

4.3.2.4. Effect of draw solute on pre-concentrated wastewater pH

For all three draw solutions, the wastewater pH gradually increased during the pre-concentration process (Figure 4.7). This is a result of the net diffusion of hydrogen ions from the feed to the draw solution. Hydrogen ion diffusion occurs in order to maintain solution electroneutrality, as a result of reverse solute flux [152, 207]. When EDTA-2Na was used, the wastewater pH tended to increase at a fractionally slower rate compared with the other two draw solutions, and may be due to the significantly lower reverse solute flux rate of EDTA-2Na. Additionally, despite the lower reverse solute flux of sodium acetate compared to sodium chloride, the basic nature of highly concentrated sodium acetate solution may have contributed to the observed high wastewater pH. Results indicate that independent of the selected draw solution, FO pre-concentrated wastewater will have a high pH (approximately pH 8) and thus may need adjustment prior to feeding into an anaerobic reactor.

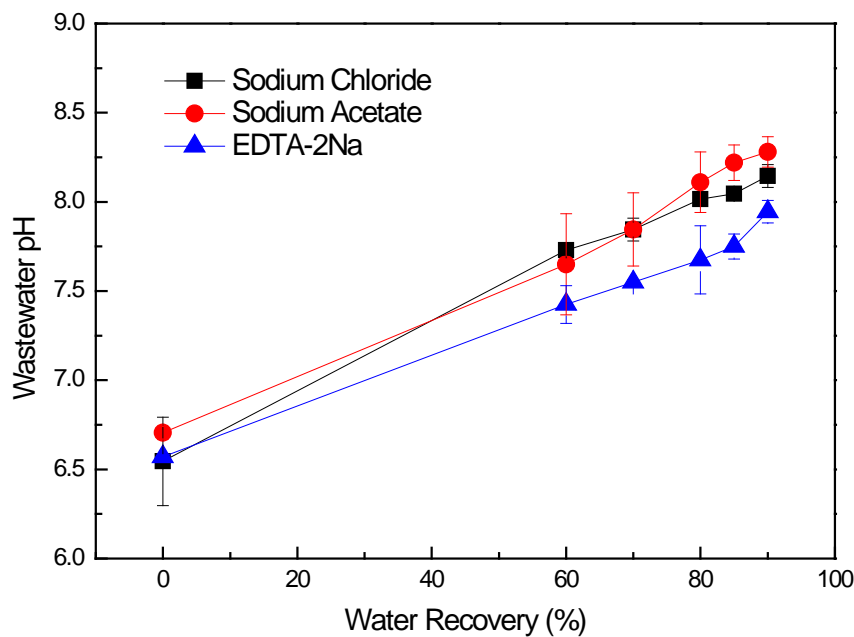


Figure 4.7. Variation of pre-concentrated wastewater pH during batch wastewater pre-concentration experiments. Experimental conditions: primary effluent feed solution (2 L); $\pi = 60$ bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s). Error bars represent the standard deviation of measurements from duplicate experiments.

4.3.3. Membrane fouling

Although FO can provide a low-fouling alternative to pressure driven membrane processes, pre-concentration of high suspended solids content wastewater inevitably leads to membrane fouling. As shown in Figure 4.8, when a cross-flow velocity of 9 cm/s was applied, severe membrane fouling was evident by a rapid water flux decline. Importantly, a water recovery of only 70% could be achieved as the water flux had reduced to below 1 L/m²h.

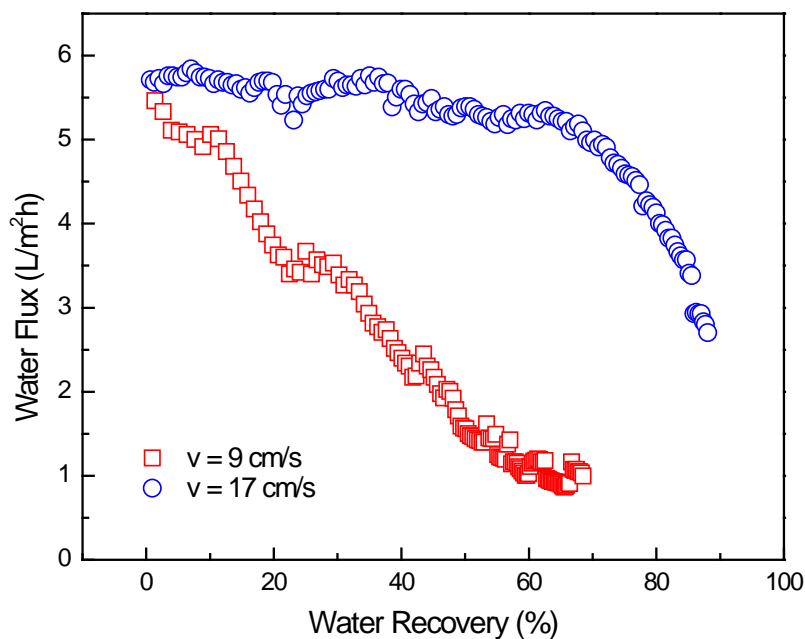


Figure 4.8. Effect of applied cross-flow velocity on water flux during the continuous flow experiment. Experimental conditions: primary effluent feed solution (5 L); $\pi = 60$ bar, NaCl draw solution; cross-flow rates of both feed and draw solutions were adjusted to achieve desired cross-flow velocity.

We increased the cross-flow velocity as a hydraulic fouling control method during the continuous flow experiment. The difference in water flux decline patterns between the two cross-flow velocities (i.e. 9 cm/s and 17 cm/s) was significant (Figure 4.8). When the cross-flow velocity was approximately doubled, water flux decline was considerably lower, and the target water recovery of 90% could be achieved in one cycle. Increasing the cross-flow velocity provides additional shear force, which hinders the accumulation of foulants on the membrane surface [92]. For the higher cross-flow velocity, the water flux decline was minimal up to a water recovery of 70%. From this point onwards, water flux declined more rapidly, most likely due to the increased solids content of the pre-concentrated wastewater at

high water recoveries. Despite the flux declining by approximately half at a water recovery of 90%, the increased cross-flow velocity was shown to effectively reduce the rate of water flux decline for the complex pre-concentrated wastewater solution. High cross-flow velocity flushing regimes can be further optimised to lower the energy consumption of this membrane fouling control strategy. However, this aspect is beyond the scope of this chapter, and further investigations are presented in the next chapter (Chapter 5).

4.3.4. Fouling reversibility and water flux sustainability

Increasing the applied cross-flow velocity resulted in less flux decline during wastewater pre-concentration. However, after one cycle, water flux still declined to approximately 50% of the initial value. After membrane flushing, the initial water flux was completely restored (Figure 4.9), demonstrating the reversibility of FO membrane fouling. Furthermore, this water flux recoverability highlights the negligible contribution of feed water salinity increase to water flux decline. The FO process inherently inhibits fouling due to the nature of the osmotic driving force. The absence of hydraulic pressure promotes a loose and highly reversible fouling layer. In addition, FO generally operates at a low water flux and therefore a lower fouling rate [63]. For these reasons, simple membrane flushing is a highly effective cleaning strategy.

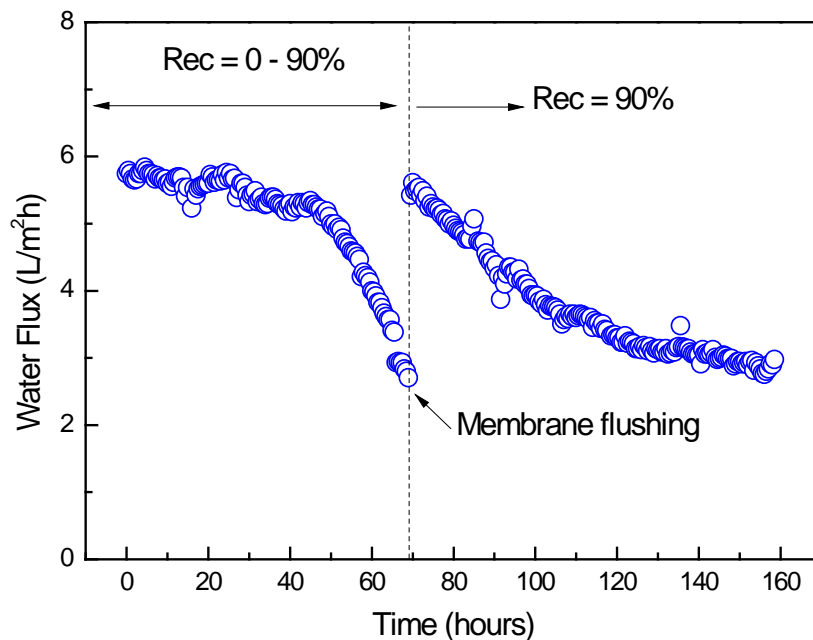


Figure 4.9. Variation of water flux during the continuous flow experiment for one pre-concentration cycle and at a fixed 90% water recovery (i.e. $\text{Rec} = 90\%$). Experimental conditions: primary effluent feed solution (5 L); $\pi = 60$ bar, NaCl draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s).

Longer-term water flux behaviour was observed by continuously operating the FO system with the pre-concentrated wastewater solution (i.e. fixed 90% water recovery) after one pre-concentration cycle. In other words, after 70 h of operation, fresh primary effluent was fed into the FO feed solution and concentrate was withdrawn to maintain a constant 90% system water recovery. From 70 h onwards, the water flux gradually declined due to the continuous exposure to the pre-concentrated wastewater. Interestingly, the rate of water flux decline gradually decreased and appeared to reach a steady state at approximately 150 h. This may indicate that the fouling cake layer had reached a maximum thickness, due to the cross-flow conditions. Nonetheless, membrane fouling remains a prominent hurdle for FO systems and further efforts are required to investigate the effectiveness of other fouling mitigation methods during wastewater pre-concentration.

4.4. Conclusions

Pre-concentration of wastewater using FO presents a feasible approach to maximise the content of organic matter and possibly improve the digestibility of wastewater. In this study, the FO system achieved a COD concentration factor of approximately eight for low and moderate strength wastewater, at a water recovery of 90%. Specifically, FO allows for the pre-concentration of wastewater to the COD range (i.e. > 1000 mg/L) suitable for biogas production via anaerobic treatment, even with low strength primary effluent obtained during wet weather. Furthermore, the importance of draw solution selection is emphasised, as ionic organic draw solutes benefited the pre-concentration process in two ways. Both sodium acetate and EDTA-2Na solutes effectively mitigated excessive salinity build-up in the pre-concentrated wastewater due to their lower reverse solute fluxes. Additionally, the ionic organic draw solutes enhanced the COD of low strength pre-concentrated wastewater, and are expected to benefit the digestibility of the solutions in terms of biogas production compared to sodium chloride. Significant membrane fouling was observed when operating at 90% water recovery using raw wastewater during the continuous flow experiment. However, this was reversible and could be controlled by optimising the hydrodynamic conditions during the FO process. Further developments of this FO wastewater pre-concentration process are recommended, including sustainable membrane fouling mitigation strategies and techno-economic evaluation at a pilot scale level.

CHAPTER 5: Physical cleaning techniques to control fouling during the pre-concentration of high suspended solid content solutions by forward osmosis

Corresponding publication:

A.J. Ansari, F.I. Hai, T. He, W.E. Price and L.D. Nghiem, Physical cleaning techniques to control fouling during the pre-concentration of high suspended solid content solutions by forward osmosis, Submitted to Desalination on 29.06.2017 (under review).

5.1. Introduction

Phosphorus is an essential fertilizer ingredient. As the supply of fossil phosphorus is dwindling, the need to develop an alternative and renewable source of phosphorus has emerged as a significant challenge of our time [37, 208-210]. The expected shortage of phosphorus is an imminent threat to all agricultural and industrial processes that rely on this valuable element [211, 212]. Comprehensive analyses of global phosphorus flows have identified wastewater discharge as a dominant pathway of non-diffuse phosphorus losses. Thus, phosphorus recovery from wastewater is a promising source of this important element [213, 214]. In addition to the future concern of phosphorus depletion, phosphorus recovery from wastewater can minimise the risk of struvite scaling on wastewater treatment equipment [215, 216] and prevent the discharge of nutrient that may cause eutrophication in natural waterways [3, 173, 217].

Several approaches have been developed to recover phosphorus from wastewater. They differ in regards to the source water and the method used to pre-concentrate phosphate. Source waters include urine [118], raw wastewater [107, 108, 218], treated effluent [114, 219], sludge [5], and digested sludge centrate (i.e. anaerobic supernatant) [30, 152, 200]. Among these source waters, digested sludge centrate is an important target for phosphorus recovery because it is small in volume but rich in phosphorus and readily available at any large scale wastewater treatment plant [30, 152, 200]. The efficiency of phosphorus recovery, generally as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) [216] can be enhanced by pre-concentrating phosphate prior to chemical precipitation. A novel membrane filtration process with significant potential for pre-concentrating phosphate for subsequent recovery is forward osmosis (FO). As a high rejection membrane process, FO can effectively retain and enrich the

phosphate and some of the ammonia in digested sludge centrate for subsequent recovery [39, 61, 63]. Furthermore, the bidirectional diffusion of protons from the feed solution into the draw solution [207] increases the digested sludge centrate pH and provides a more favourable alkaline environment for chemical phosphorus recovery [152, 200].

FO can be used to extract clean water from difficult and complex waste streams that could not be processed by other conventional filtration processes. Previous studies have demonstrated the low fouling propensity of FO compared with its pressure driven counterparts such as reverse osmosis (RO) [51, 53, 103]. More importantly, FO membrane fouling appears to be reversible [51, 53, 103]. Indeed, several lab and pilot scale tests of FO membranes for the treatment of these highly complex waste streams including fracking fluid [220, 221], drilling mud [222], landfill leachate [223], and digested sludge centrate [152, 200] have been reported. In particular, the results obtained in Chapter 4 have highlighted the challenge of controlling fouling during the pre-concentration of the high suspended solid content sludge centrate solution. Nevertheless, no previous studies have comprehensively evaluated the FO process for a high water recovery (>80%) from digested sludge centrate that is necessary to achieve viable phosphorus recovery [224]. Thus, techniques to mitigate and control fouling are essential for realising the full potential of FO for high suspended solids waste streams, such as digested sludge centrate [50, 225].

FO membrane fouling can be controlled via either a physical or chemical cleaning process [81, 226]. Physical cleaning techniques such as cross-flow velocity increase or pulsated cross-flow, membrane flushing, air-scouring, osmotic backwashing, and ultrasonication have been studied for different applications and FO configurations [92, 162, 227, 228]. These techniques provide vigorous hydrodynamic conditions to prevent or remove the fouling cake layer from the membrane surface [92, 103]. FO membrane fouling during the pre-concentration of sludge centrate is expected to occur rapidly but also be readily reversible. Thus, although chemical cleaning can be much more effective than physical cleaning [229, 230], it is not compatible with the high cleaning frequency necessary for pre-concentrating sludge centrate for subsequent phosphorus recovery. In this context, ultrasonication is a promising technique to complement other physical cleaning techniques. Indeed, the potential of ultrasonication as a robust but chemical free FO cleaning technique has recently been demonstrated for calcium sulfate scaling [228] and supernatant from waste activated sludge thickening [227].

Previous investigations have demonstrated the capability of FO to effectively retain thus pre-concentrate phosphate in the sludge centrate by more than five times [152, 200] to further enhance the economic viability of phosphorus recovery. Preliminary results from these investigations on fouling assessment also highlight the need to develop an effective membrane cleaning strategy to counteract the rapid but potentially more reversible fouling during the pre-concentration of sludge centrate by FO.

This chapter evaluates the propensity and characteristics of FO membrane fouling for phosphorus recovery applications. Accelerated fouling conditions are applied to represent the long-term and intensive concentration scenario that is required for phosphorus recovery. We investigate three physical membrane fouling control techniques, namely, in-situ membrane flushing, air-scouring, and ultrasonication. Techniques are evaluated based on water flux decline and recoverability.

5.2. Materials and methods

5.2.1. Materials and chemicals

The cellulose triacetate FO membrane was from Hydration Technologies, Inc. (Albany, Oregon, USA). Analytical grade NaCl was used as the draw solute at a concentration of 3 M. Wastewater was obtained after primary sedimentation from the Wollongong Water Recycling Plant (New South Wales, Australia). The sludge centrate was obtained from a digested sludge dewatering centrifuge from the same plant.

5.2.2. Forward osmosis system

A lab-scale, cross-flow FO system was employed in this study. The cell was constructed of two symmetric flow channels with length, width, and height dimensions of 100 mm, 50 mm, and 3 mm, respectively, and an effective membrane area of 50 cm². Circulation of the feed and draw solutions through the cell flow channels was achieved by two variable speed gear pumps (Micropump, Vancouver, Washington, USA). The circulation flow rate was regulated using two rotameters, and pump speed was adjusted to achieve the desired cross-flow velocity. For all experiments, a spacer was positioned on the draw solution side of the membrane cell to improve draw solution mixing. The flat-sheet membrane was sandwiched between two rubber gaskets and the two perspex semi-cells. The feed solution was circulated along the top semi-cell unless otherwise stated.

Permeate water flux was determined by recording the weight changes of the draw solution tank using a digital balance (Mettler-Toledo Inc., Hightstown, New Jersey, USA) at two minute intervals. Calculation of water flux was performed according to a standard procedure described elsewhere [186]. All experiments were conducted using a constant 3 M NaCl draw solution. The draw solution concentration (therefore osmotic pressure) was maintained constant using a conductivity controlled pump, which dosed highly concentrated stock solution (5 M) of NaCl into the draw solution. Conductivity was continuously measured using a conductivity probe (Cole-Parmer, Vernon Hills, Illinois, USA), and was connected to a controller and a peristaltic pump to regulate the concentration of the draw solution (control accuracy of ± 0.1 mS/cm). The temperature of the system was maintained at 21 °C using a chiller and heater during all experiments (Neslab RTE 7, Thermo Scientific, Waltham, MA).

5.2.3. Cleaning Equipment

Three fouling control techniques were evaluated in this study. They include in-situ flushing, air-scouring, and ultrasonication. In-situ flushing was achieved by increasing the circulation flow rates of the feed and draw solutions. The schematics of the air-scouring and ultrasonication cleaning equipment, and their assimilation with the FO system are shown in Figure 5.1. Each fouling control technique was applied separately, either continuously for fouling prevention or intermittently for membrane cleaning. The former does not interrupt the FO process. The latter requires a brief suspension of the FO process for foulant removal using clean water.

For in-situ flushing, the pump circulation flow rate was adjusted to increase the rate of cross-flow velocity flushing (i.e. five times the baseline cross-flow velocity). Air-scouring was achieved by connecting an air pump (Aqua One, Australia) inline to the cross-flow membrane cell entry tube, via a one way valve (Figure 5.1A). The air supply rate was adjusted to achieve a uniform mixture of water and air (approximately 3 L/min). For ultrasonic application, the membrane cell was immersed inside a low frequency (i.e. 30 kHz) ultrasonic water bath (ECO-CT, Ultrasonics Eco, Queensland, Australia) (Figure 5.1B). The gaskets and tight screws of the membrane cell prevented leakage of liquid from the water bath (i.e. DI water) into the membrane cell flow channels and was verified by clear water testing. The temperature of the ultrasonic bath was maintained at 21 °C using a cooling loop. The cooling loop consisted of a separate reservoir with a submerged stainless steel heat-exchanging coil connected to a chiller (SC200-PC, Aqua Cooler, Sydney, Australia), and a peristaltic pump to circulate liquid between the water bath and cooling reservoir.

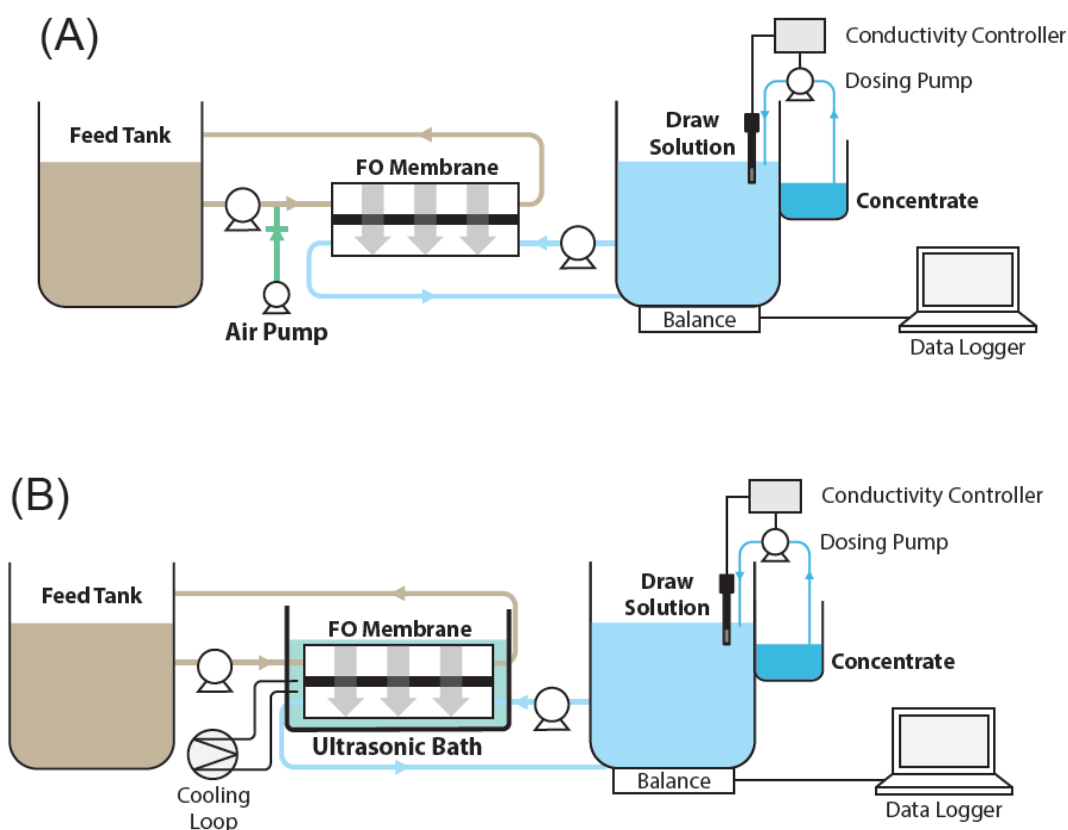


Figure 5.1. Schematic representation of an FO system with (A) air-scouring and (B) ultrasonication cleaning equipment.

5.2.4. Accelerated fouling experimental protocol

Accelerated fouling conditions were implemented by applying a high draw solution concentration to maximise water flux and therefore increase the rate of membrane fouling. The circulation flow rate for all reference experiments (i.e. without applying physical cleaning) was 0.5 L/min (corresponding to a cross-flow velocity of 8.3 cm/s). An analytical grade NaCl solution of 3 M was used as the draw solution and this concentration was kept constant throughout the experiment using an automated control system [121]. A preliminary experiment using a synthetic solution with similar background electrolytes to the sludge concentrate was also conducted. The water flux was constant over the entire experiment of 12 hours suggesting that the increase in osmotic pressure of the feed was insignificant. Since the draw solution concentration was constant and the increase in the feed osmotic pressure was insignificant, any observable flux decline in this study can be solely attributed to membrane fouling.

All experiments were performed with the membrane oriented in FO mode (i.e. active layer facing the feed solution) and in a counter-current flow arrangement. The feed solution volume was 1.5 L and the initial draw solution volume was 1 L.

5.2.5. Physical cleaning

The three fouling control techniques described in section 5.2.3 were applied either continuously for membrane fouling prevention or intermittently for membrane cleaning. For membrane fouling prevention, these techniques were continuously applied during the entire accelerated fouling cycle. The water flux obtained was then compared with the reference condition (i.e. circulation flow rate of 0.5 L/min, corresponding to a cross-flow velocity of 8.3 cm/s).

For membrane cleaning, an accelerated membrane fouling experiment was first conducted. After each fouling cycle (approximately five hours) the membrane was cleaned for 30 minutes in-situ using one or a combination of these techniques with DI water as the carrier fluid. After cleaning, flux recoverability was determined by replenishing the feed solution with fresh digested sludge centrate. High cross-flow flushing was achieved by increasing the circulation flow rate by five-fold (i.e. 42 cm/s), whilst, the other cleaning techniques were analysed at the reference flow rate for comparison. Repetitive membrane cleaning was performed by operating consecutive four hour accelerated fouling cycles. At the conclusion of each cleaning cycle, the feed solution was replaced with fresh sludge centrate.

5.2.6. Membrane autopsy

Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) (JCM-6000, JEOL, Tokyo, Japan) was used to identify the fouling layer morphology and composition. The membrane samples were firstly air-dried in a desiccator and then coated with an ultra-thin gold layer with a sputter coater (SPI Module, West Chester, PA).

5.2.7. Analytical methods

The water quality parameters of the wastewater and primary effluent were measured following standard procedures. Total organic carbon (TOC) was analysed using a Shimadzu analyser (TOC-V_{CSH}) and key ions were analysed using an inductively coupled plasma – optical emission spectroscopy (ICP-OES) system (ICP-OES 710, Agilent, Australia). The temperature, pH, and electrical conductivity were monitored using an Orion 4-Star pH/conductivity meter (Thermo Scientific, Waltham, MA).

5.3. Results and discussion

5.3.1. Fouling propensity of wastewater and digested sludge centrate

The fouling propensity of raw wastewater and digested sludge centrate was evaluated by performing FO filtration experiments under accelerated fouling conditions (Figure 5.2). As noted in section 5.2.5, water flux decline can be solely attributed to membrane fouling since the draw solution was maintained at 3 M NaCl and osmotic pressure increase in the feed solution was negligible. For raw wastewater, the water flux gradually declined by approximately 42% of its initial value after 12 hours of operation. On the other hand, digested sludge centrate showed a more severe fouling behaviour, with a sharp initial decrease and total water flux decline of 86% after 12 hours. Under these accelerated fouling conditions, water recoveries from raw wastewater and sludge centrate were approximately 50 and 21%, respectively. Compared to digested sludge centrate, the observed water flux decline when raw wastewater was pre-concentrated was less significant. Thus, sludge centrate was used in all subsequent experiments to evaluate the effectiveness of physical cleaning.

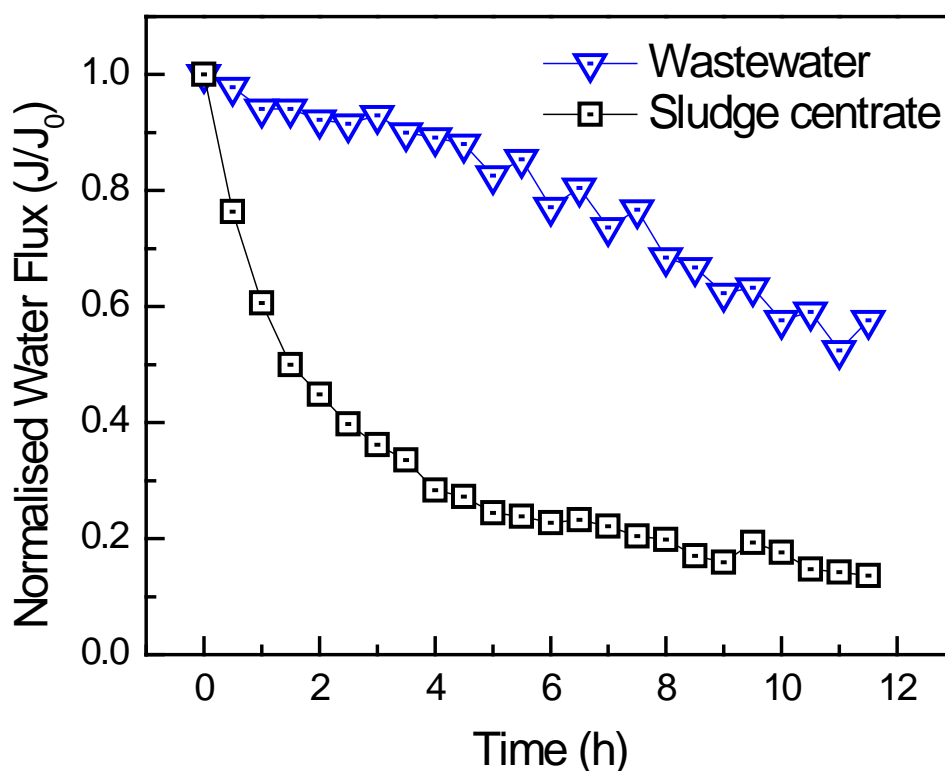


Figure 5.2. Comparison of wastewater and digested sludge centrate fouling propensity. Fouling propensity is represented as the observed water flux decline during accelerated fouling conditions. Initial water flux of wastewater and digested sludge centrate was $20.0 \pm 0.5 \text{ L/m}^2\text{h}$. Accelerated fouling conditions: feed solution was either wastewater or digested sludge centrate; NaCl draw solution was maintained at 3 M; cross-flow rates of both the feed and draw solutions were 0.5 L/min (corresponding to a cross-flow velocity of 8.3 cm/s).

The high fouling propensity of sludge centrate can be attributed to its very high solids (i.e. 1.16 g/L) and mineral content (i.e. calcium and magnesium) as can be seen in Table 5.1. For digested sludge centrate, during the first two hours of FO filtration, the water flux declined rapidly, possibly due to the significant deposition of solid particles on the membrane surface. After this point, the rate of water flux decline was much smaller. The flux profile in Figure 5.2 suggests that rapid cake layer formation was the prevalent cause of FO membrane fouling. The formation of a cake layer on the membrane surface can result in severe cake-enhanced concentration polarisation, thus, reducing the effective osmotic driving force. It is noteworthy that major constituents in the sludge centrate including phosphate, ammonia and dissolved organics can be effectively retained by the FO process (Table 5.1). This attribute is essential for subsequent resource (phosphorus in this example) recovery but can also aggravate the cake-enhanced concentration polarisation phenomenon [224].

Table 5.1. Characteristics of raw wastewater and digested sludge centrate (average concentration \pm standard deviation from triplicate measurements). The minimum FO rejection was calculated based on experimental data from our previous study [200].

Parameter	Units	Raw wastewater	Sludge centrate	Sludge centrate - Minimum FO rejection (%)
Total solids	g/L	0.64 ± 0.03	1.16 ± 0.03	-
Volatile solids	g/L	0.40 ± 0.02	0.58 ± 0.12	-
Electrical conductivity	mS/cm	1.45 ± 0.24	5.99 ± 0.11	-
pH	-	6.85 ± 0.10	7.77 ± 0.05	-
Total organic carbon	mg/L	45 ± 10	602 ± 16	94.3
Total nitrogen	mg/L	41 ± 9	764 ± 25	67.6
$\text{PO}_4^{3-}\text{-P}$	mg/L	23 ± 5	97 ± 7	98.6
$\text{NH}_4^+\text{-N}$	mg/L	71 ± 12	521 ± 22	88.3
Ca^{2+}	mg/L	-	63 ± 5	-
Mg^{2+}	mg/L	-	14 ± 5	-
K^+	mg/L	-	106 ± 3	-

5.3.1.1. Digested sludge centrate fouling characterisation

Representative morphology and composition of the sludge centrate fouling layer are shown in Figure 5.3. The presence of irregular sized crystals suggests the dominance of inorganic membrane fouling (Figure 5.3A). Elementary analysis results indicated that the crystals predominantly contained carbon, oxygen, magnesium, phosphorus, and calcium (Figure 5.3B). Some crystals resembled an orthorhombic like shape typical of struvite,

however, the presence of calcium and organic matter in solution was likely to influence the crystal size, shape, and purity. Interestingly, visual observation of the fouling layer on the membrane coupon revealed a white flaky precipitate layer at the centre and a brown area at the edge of the membrane coupon (Figure 5.3C). The presence of these two distinctive fouling areas is likely due to the hydraulic profile within the membrane cell. In other words, the brown sections indicate areas where suspended organic solids were more likely to accumulate. Nevertheless, detailed examination by SEM analysis revealed no discernible difference in the morphology and composition of these two areas.

The observed crystal morphology and the rapid flux decline shown in Figure 5.2, suggest that bulk crystallization of minerals occurred in the digested sludge feed solution, followed by particle deposition on the membrane surface [231]. However, it is noted that under the accelerated fouling condition in this experiment, the water recovery was only 21%. Thus, the deposition of more mineral crystals would be expected at higher water recoveries. As previously mentioned, in phosphorus recovery applications, a high concentration factor is necessary to improve process performance (i.e. phosphorus precipitation kinetics) and economics (i.e. chemical consumption) [152, 200].

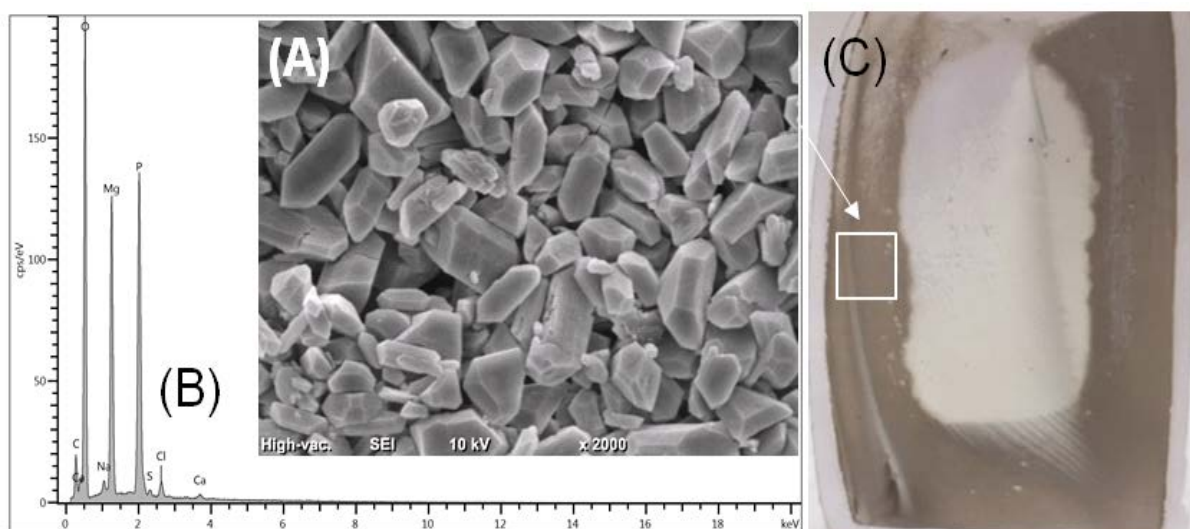


Figure 5.3. (A) SEM micrograph and (B) EDS spectra of the FO membrane surface at the conclusion of the accelerated fouling experiment using digested sludge centrate as the feed solution. Experimental conditions are described in Figure 5.2.

5.3.2. Membrane fouling prevention

Three fouling prevention techniques were evaluated during the pre-concentration of digested sludge centrate using FO. These prevention techniques were continuously applied

during the accelerated fouling cycle and each presented a unique effect on water flux decline compared to the reference flux decline (i.e. when no prevention technique was applied) (Figure 5.4).

Operating at a high cross-flow velocity (i.e. 42 cm/s or five times the reference cross-flow velocity of 8.3 cm/s) and ultrasonic application effectively slowed the rate of water flux decline (Figure 5.4). Similarly, constant ultrasonic application reduced the severity of water flux decline compared to the reference. Increasing the cross-flow velocity is a proven technique to improve the hydrodynamic conditions close to the membranes surface as turbulence and shear force can prevent foulant accumulation [92]. On the other hand, the observed benefit of applying ultrasonication was possibly due to the combined effects of induced cavitation and the agitation of foulants near the membrane surface [232]. Ultrasonic application also reduced the extent of concentration polarisation by rapidly mixing both the feed and draw solutions close to the membrane surface, and thus improving the water flux dynamics [233]. Our results are consistent with previous studies on membrane cleaning using ultrasonication [227, 228, 234].

In contrast, air-scouring had a negative effect during the five hour fouling cycle. Water flux decline during continuous air-scouring was more severe than the reference condition. Within the first 30 minutes, water flux did not decline dramatically. However, after the first 30 minutes, water flux drastically declined as air bubbles appeared to compress the fouling layer within the narrow membrane feed channel of the cross-flow module. The presence of air bubbles along the membrane surface may also reduce the available surface area (where the feed solution is in contact with the membrane for mass transfer), thus, limiting the rate of water permeation through the membrane. This effect was verified by performing the experiment with the feed active layer facing up and facing downwards in the membrane cell. Negligible differences in water flux decline were observed between the two configurations (data not shown). Air-scouring as a fouling prevention technique is generally a successful option in membrane bioreactor applications [235]. Our results suggest that module configuration is an essential parameter to consider when applying air-scouring, alongside aeration intensity, optimum bubble size and membrane contact [236]. Applying air-scouring for membrane fouling prevention is expected to be more viable in a submerged membrane configuration.

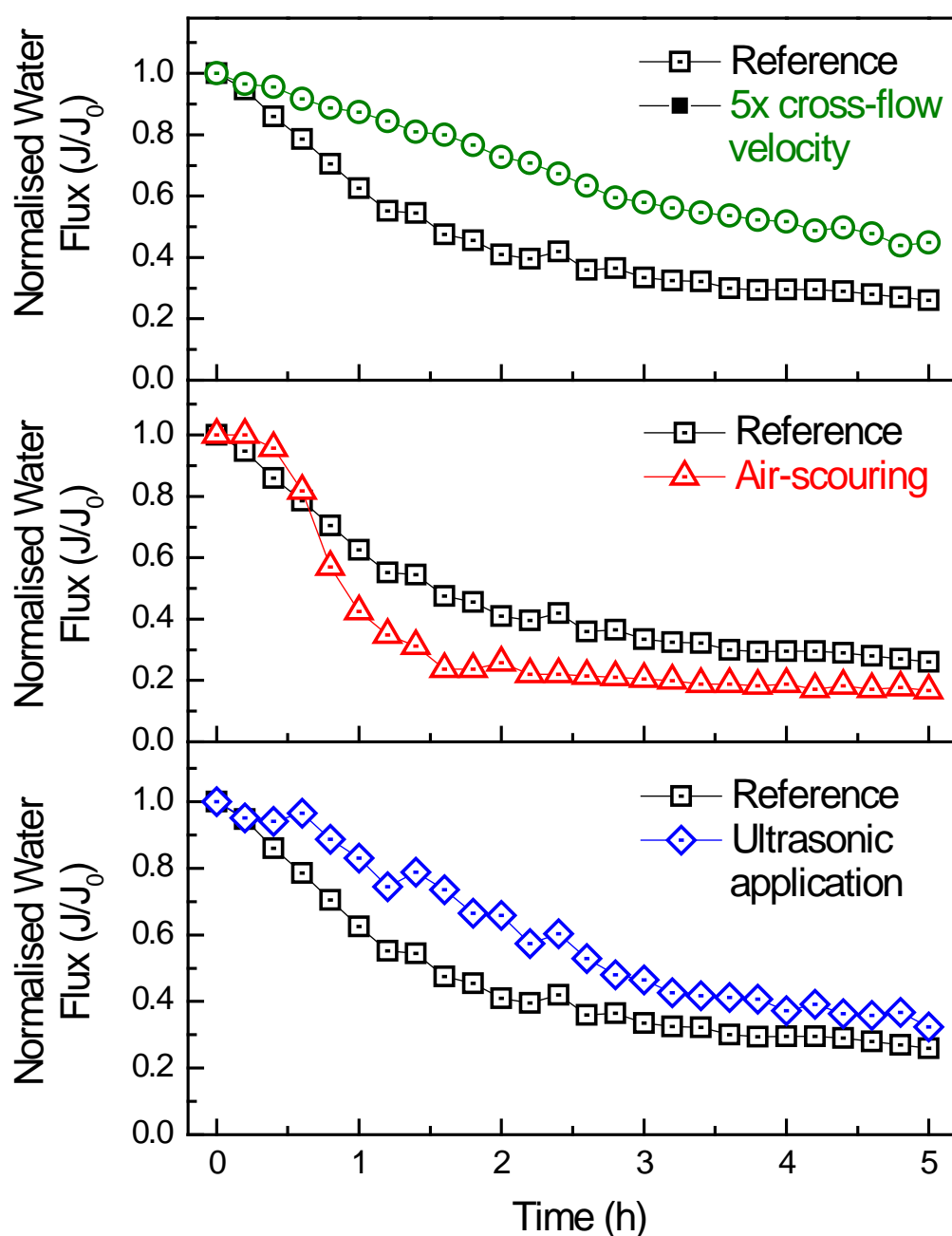


Figure 5.4. Normalised water flux decline during accelerated fouling conditions with; (A) 5x cross-flow velocity (i.e. 42 cm/s), (B) air-scouring, and (C) ultrasonic application, applied as fouling prevention techniques. Prevention techniques were continuously applied during the filtration time. Reference condition represents fouling cycle under accelerated fouling conditions. Accelerated fouling conditions: feed solution was digested sludge centrate; NaCl draw solution was maintained at 3 M; cross-flow rates of both the feed and draw solutions were 0.5 L/min (corresponding to a cross-flow velocity of 8.3 cm/s).

Increasing the cross-flow velocity during filtration cycles was the most effective strategy amongst the three techniques investigated here. This achieved the highest cumulative

permeate volume during the five hour cycle corresponding the lowest water flux decline. Variations in the cross-flow velocity rate are expected to be proportional to the water flux behaviour, however, this would correspondingly influence the systems energy consumption. Costs associated with circulation can be significant for FO membrane systems [113] and therefore optimisation of membrane fouling prevention techniques is important for a sustainable system. A similar argument can be said for ultrasonication, as continuous application would not be feasible due to the extensive energy consumption required.

5.3.3. Membrane cleaning

5.3.3.1. Influence of repetitive high cross-flow velocity flushing

The promising results of high cross-flow velocity and ultrasonication were further investigated for membrane cleaning. At the conclusion of each accelerated fouling experiment, in-situ high cross-flow velocity flushing with DI water could restore the water flux to the initial value (Figure 5.5). In comparison to the results in Figure 5.4A, these results (Figure 5.5) show that applying membrane cleaning is more effective than solely implementing fouling prevention over the five hour period. During the 30 minute cleaning period, foulants on the membrane surface were dislodged and removed from the membrane surface. Furthermore, since the feed and draw solutions were replaced with DI water, there was no water permeation during membrane cleaning. This relaxation period could also improve the effectiveness of high cross-flow velocity induced shearing on the fouling layer. Since membrane cleaning can be as short as 30 mins, this approach results in a lower energy requirement and only a brief suspension of the filtration process compared to continuous operation at a high cross-flow velocity.

There was evidence that high cross-flow velocity flushing could not completely remove all solid particles from the membrane surface. Thus, it was not sustainable over multiple cycles of repetitive cleaning during accelerated digested sludge centrate fouling (Figure 5.6). At the conclusion of each cleaning cycle, the feed solution was replaced with fresh sludge centrate and a graduate flux decline was observed after several consecutive cleaning cycles. These results indicate that the effectiveness of high cross-flow velocity cleaning is dependent on cleaning frequency.

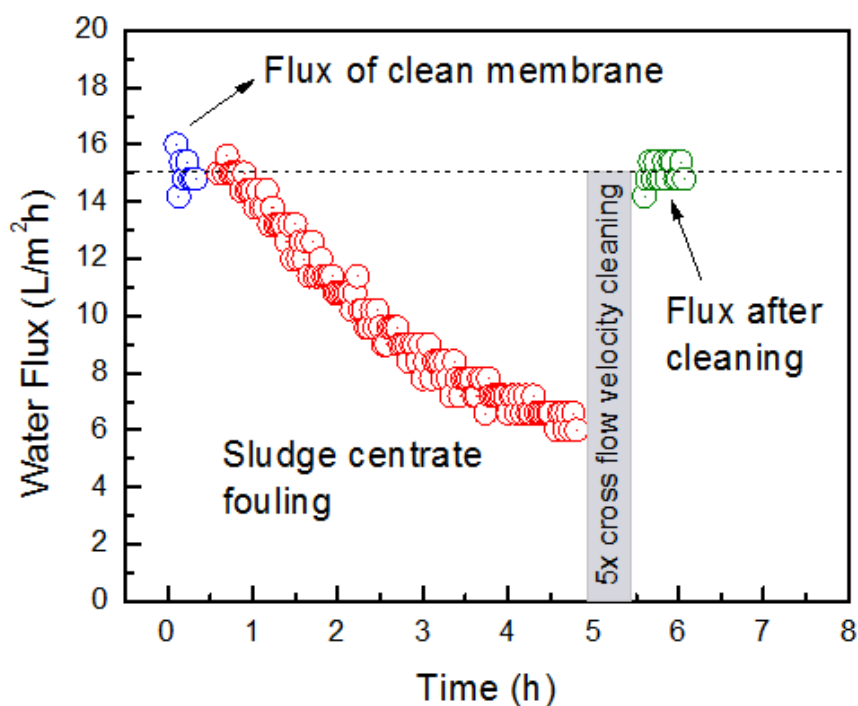


Figure 5.5. Water flux decline profile for a single digested sludge centrate fouling cycles using 30 minutes in-situ high cross-flow velocity flushing (i.e. 42 cm/s) with DI water. Accelerated fouling conditions: feed solution was digested sludge centrate; NaCl draw solution was maintained at 3 M; cross-flow rates of both the feed and draw solutions were 0.5 L/min (corresponding to a cross-flow velocity of 8.3 cm/s).

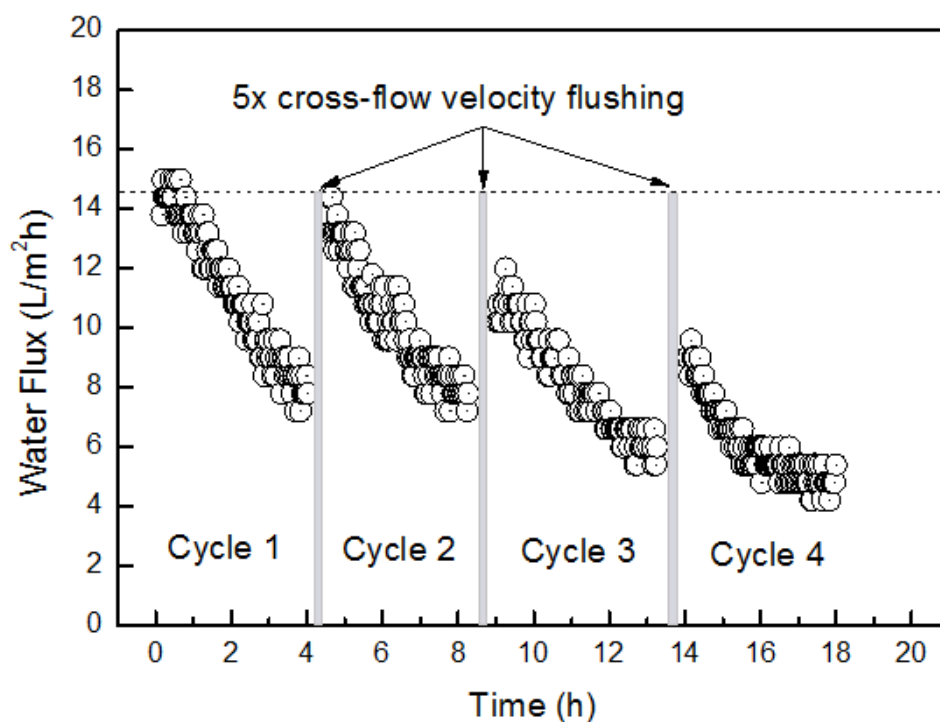


Figure 5.6. Water flux decline profile for repetitive, digested sludge centrate accelerated fouling cycles using 30 minutes in-situ high cross-flow velocity flushing (i.e. 42 cm/s) with DI water. Experimental conditions are as in Figure 5.5.

5.3.3.2. Complementary effects of ultrasonic cleaning and high cross-flow velocity flushing

Given the effectiveness of ultrasonication to prevent fouling during accelerated fouling condition (Section 5.3.2), the combination of ultrasonic cleaning and high cross-flow velocity flushing was evaluated for membrane cleaning. Both the reference and five times the cross-flow velocity were analysed to quantify the individual and complementary effects of these two cleaning techniques. The duration of the accelerated fouling cycle was increased to approximately 20 hours, to clearly distinguish the effectiveness of each cleaning strategy. Figure 5.7A & B show how cross-flow velocity flushing at varying intensities was insufficient to restore the initial water flux after a 20 hour fouling cycle. On the other hand, ultrasonic application improved the water flux recovery at both rates of cross-flow velocity (Figure 5.7C and D). The complementary effects of the two cleaning techniques were evident by the near complete restoration of water flux after ultrasonic application combined with high cross-flow velocity flushing (Figure 5.7D). The foulant material released from the membrane surface as a result of ultrasonication (i.e. high shear and turbulent conditions caused by cavitation) were more readily transferred into the bulk cleaning fluid (i.e. DI water) due to the high cross-flow velocity environment. Ultrasonic cleaning significantly improved simple membrane flushing and has the potential to reduce the frequency of chemicals used for FO membrane cleaning.

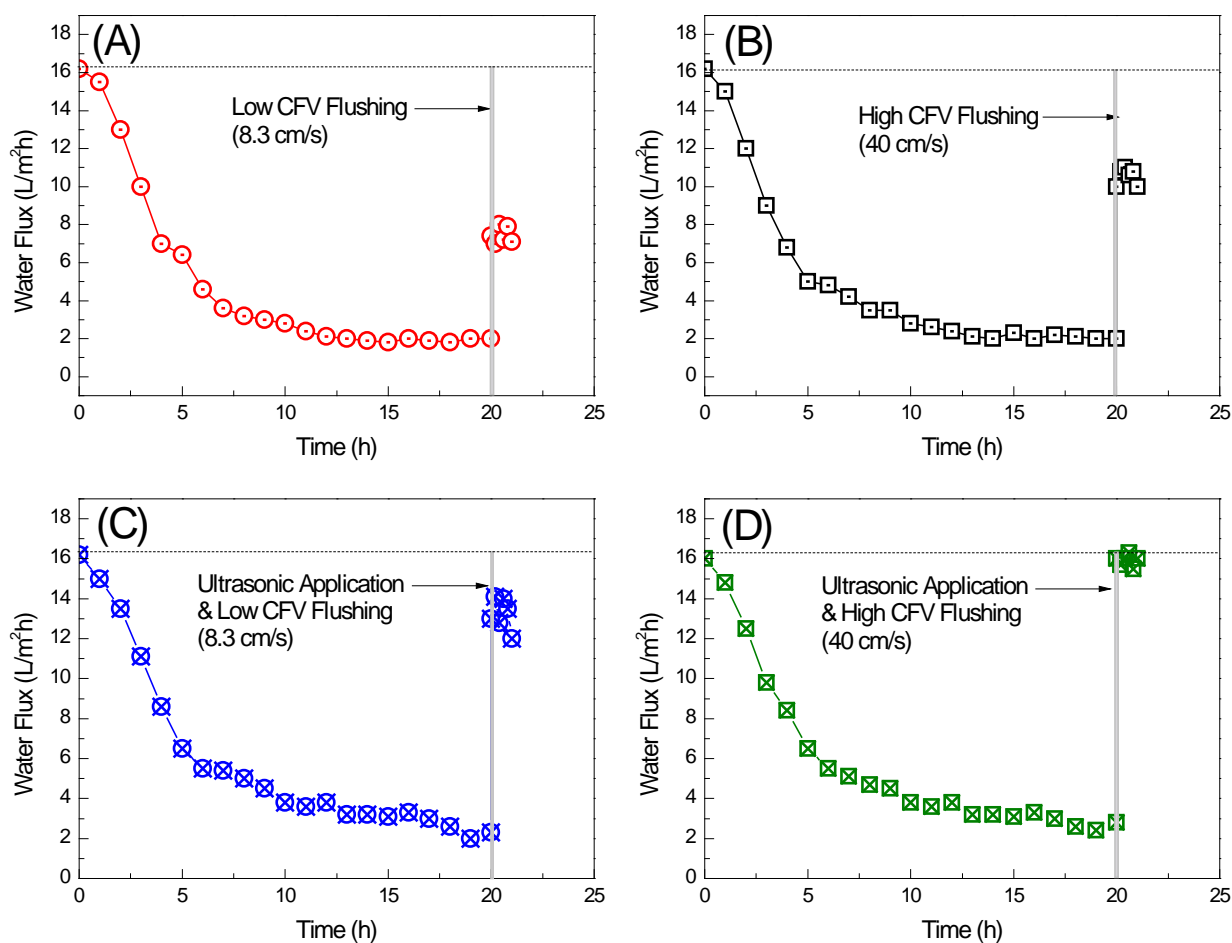


Figure 5.7. Accelerated fouling profile and water flux recovery after applying 30 minutes of (A) low cross-flow velocity (CFV), (B) high cross-flow velocity, (C) ultrasonic application with low cross-flow velocity, and (D) ultrasonic application with high cross-flow velocity. Experimental conditions are as in Figure 5.5.

The combination of ultrasonic cleaning with high cross-flow velocity flushing could recover water flux to the initial value, over four repetitive fouling/cleaning cycles (Figure 5.8). These results indicate that the combination of ultrasonication and high cross-flow velocity flushing is an effective cleaning strategy. Further evaluation of ultrasonic frequency, intensity, and other operational parameters are necessary to further demonstrate process suitability and energy consumption. It is also necessary to evaluate the long term effects of ultrasonication on membrane durability after repetitive cleaning cycles.

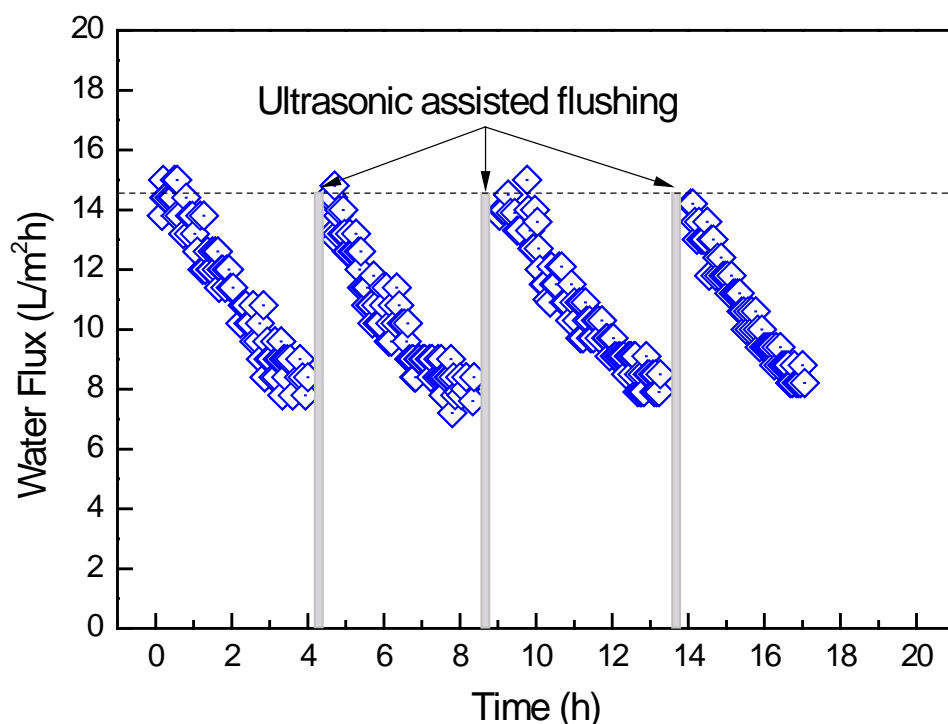


Figure 5.8. Water flux decline profile for repetitive, digested sludge centrate accelerated fouling cycles using 30 minutes in-situ high cross-flow velocity flushing (i.e. 42 cm/s) and ultrasonic application with DI water. Experimental conditions are as in Figure 5.5.

The cleaning efficiency of ultrasonic assisted flushing is also demonstrated by comparing the pristine membrane, with the fouled and cleaned CTA membrane (Figure 5.9). A detailed discussion of the digested sludge centrate fouling characterisation is presented in Section 5.3.1.1. Overall, the SEM micrographs show that the application of ultrasonication with high cross-flow velocity can significantly remove all of the crystals evident in the fouling layer (Figure 5.9C). Furthermore, this also confirms that the dominant fouling mechanisms was bulk crystallization of minerals, followed by particle deposition on the membrane surface, as physical cleaning was capable of removing the majority of foulants [231]. In terms of the EDS spectra, the cleaned membrane indicated that traces of silicon, chlorine, and potassium remained sparsely attached to the membrane surface after the four accelerated fouling cycles (Figure 5.9 C). It is possible that intensified physical cleaning or chemical cleaning may be necessary to completely restore membrane performance in long term operations.

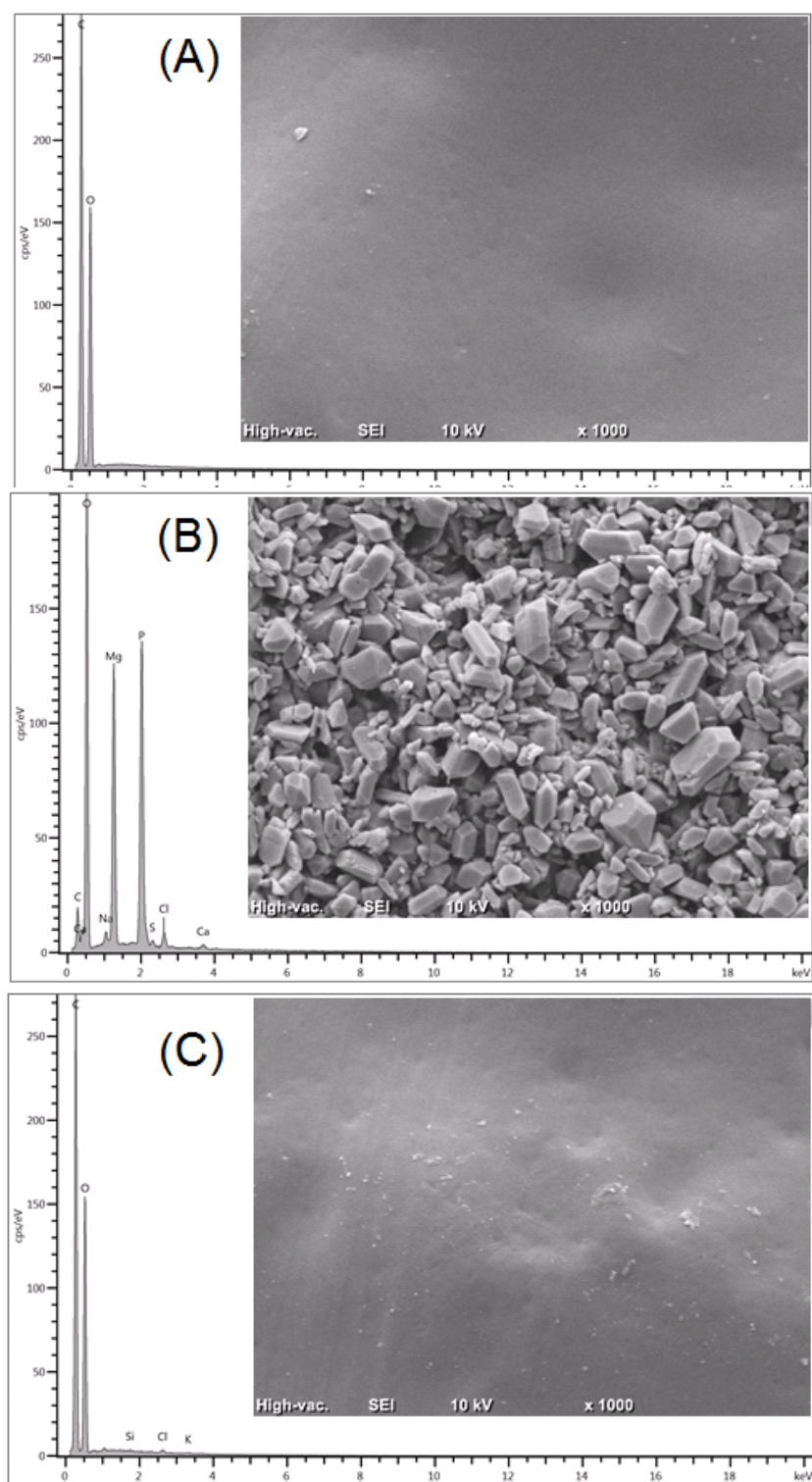


Figure 5.9. SEM micrographs and EDS spectra of the (A) pristine FO membrane, (B) fouled membrane, and (C) membrane after ultrasonic assisted flushing cleaning. Experimental conditions are described in Figure 5.8.

5.4. Conclusions

Results from this study demonstrate that forward osmosis (FO) fouling associated with the pre-concentration of digested sludge centrate for subsequent phosphorus recovery is attributed mostly to the deposition of small mineral crystals and particulate matter on the membrane surface. Thus, FO fouling during the pre-concentration of digested sludge centrate can be effectively mitigated by physical cleaning. Under accelerated fouling conditions, high cross-flow velocity flushing and ultrasonication could prevent membrane fouling to some extent, whilst air-scouring aggravated the extent of membrane fouling. The results show that periodic membrane cleaning (i.e. brief suspension of the filtration process for membrane cleaning with water) was more practical than physical fouling prevention (i.e. continuously applying control technique during filtration operation). The combination of ultrasonication and high cross-flow velocity flushing could restore water flux to the initial value over several repetitive fouling and cleaning cycles.

CHAPTER 6: Integrating forward osmosis with anaerobic treatment for simultaneous wastewater treatment and resource recovery: process performance and challenges

6.1. Introduction

Wastewater is increasingly considered as a source of water, energy, and nutrients, rather than a waste. As such, there is a growing demand for low impact wastewater treatment, aiming to prevent nutrient release into the environment and to offset the energy requirements of treatment through net positive energy generation [3, 7, 237]. This demand has driven the development of innovative technologies to tap into the significant resource potential of wastewater [39, 224, 237]. Membrane-based technologies have been essential for advanced water purification for reuse applications [6]. To the same effect, anaerobic digestion is considered to be a key technology for the realisation of energy and nutrient recovery from wastewater [14, 32, 42, 45].

Anaerobic treatment is a promising approach to replace electricity consumption (which is a secondary form of energy) by a primary energy source (e.g. thermal energy). The conventional activated sludge process consumes significant amounts of electrical energy for aeration, thus, processes that avoid aeration (such as anaerobic biological treatment) are more preferable. One challenge that significantly lowers the biogas recovery and thus economic viability of anaerobic digestion is the low strength of wastewater. Slow-growing anaerobic microorganisms are unable to effectively convert chemical oxygen demand (COD) into methane at low organic loading rates. In addition, methane loss due to dissolution in the effluent is significant at a low production rate. For low strength wastewater, processes that pre-concentrate COD and nutrients (e.g. phosphorus) are necessary to improve the economics of biogas recovery from anaerobic treatment units [46, 238].

Forward osmosis (FO) can be strategically utilised to provide a unique approach to achieve simultaneous wastewater treatment and resource recovery [104, 224]. The key advantages of FO compared to other membrane processes include, low fouling propensity and easy cleaning, low hydraulic pressure operation, and high rejection of a broad range of contaminants. FO can be coupled with membrane distillation (MD) to directly extract clean water from raw wastewater, while simultaneously concentrating wastewater for integration with anaerobic treatment. Anaerobically digesting FO pre-concentrated wastewater can

produce biogas, which can then be used by a combined heat and power engine to produce electricity and thermal energy. While surplus electricity can be supplied to the grid, the thermal energy produced can be used to power MD and the anaerobic process itself. The anaerobic process also converts biologically bound phosphorus into a soluble form, thus allowing phosphorus recovery as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) [152] or hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) [200].

Interest in combining FO with the anaerobic process has significantly increased in recent years due to the potential advantages of a low-energy wastewater stabilisation and resource recovery. Recent studies have investigated FO-anaerobic integration in terms of draw solution selection [58, 239, 240], process configurations [241-243], membrane cleaning [230], trace organic contaminant removal [244], microbial composition [166, 245], and energy dynamics [246]. The majority of these studies adopt a membrane bioreactor configuration, whereby the FO membrane is physically located within the anaerobic bioreactor (i.e. anaerobic osmotic membrane bioreactor (An-OMBR)). An alternative option involves the direct FO filtration of wastewater, whereby organic matter and nutrients are pre-concentrated and subsequently anaerobically digested. A key benefit of direct FO filtration is that the FO membrane is in contact with concentrated wastewater, which has a lower fouling propensity compared with the mixed liquor inside an An-OMBR [149, 224]. Furthermore, the volume of digestate that requires heating would be significantly less in the direct FO configuration. Nonetheless, the influence of the FO process on anaerobic digestion would be similar to some extent for both the An-OMBR and FO pre-concentration scenario.

The most prominent challenge associated with integrating FO with anaerobic treatment is the incompatibility of salinity with sensitive anaerobic microorganisms. Salinity accumulation is an inherent issue associated with the FO process, due to the reverse flux of draw solutes into the filtrate (i.e. pre-concentrated wastewater or bioreactor) as well as due to the high membrane retention of the naturally existing dissolved solutes in wastewater. In addition to lowering the FO system efficiency, the high salinity levels in anaerobic treatment systems has shown negative effects on system performance in terms of microorganism health, pollutant removal efficiency, and ultimately biogas production [57, 239, 240]. A few notable approaches to address the issue of salinity accumulation when integrating FO with anaerobic treatment have recently been proposed in the literature. Draw solution selection has shown to significantly influence process performance in terms of salinity accumulation in the FO system and anaerobic compatibility [58, 239, 240]. Furthermore, a microfiltration assisted

An-OMBR has been developed and intends to maintain an acceptable salinity level in the bioreactor [242].

This chapter aims to evaluate the process performance and investigate the key challenges associated with integrating FO with anaerobic treatment, using optimised parameters. Specifically, this study optimises the FO concentration factor (i.e. system water recovery) to balance the organic content and salt concentration in pre-concentrated wastewater and their combined effects on methane production. Based on the results shown in Chapter 3, two draw solutes namely sodium chloride (NaCl) and sodium acetate (NaOAc) are compared in terms of FO membrane performance and the digestibility of pre-concentrated wastewater. Optimised parameters and cleaning techniques are applied to mitigate salinity accumulation (i.e. alternative draw solute) and membrane fouling (i.e. physical cleaning), whilst assessing their long-term effectiveness.

6.2. Materials and methods

6.2.1. Materials and chemicals

Wastewater (effluent following primary sedimentation) and digested sludge were obtained from the Wollongong Water Recycling Plant (New South Wales, Australia). This real wastewater was used as a feed solution for FO pre-concentration experiments, whilst the digested sludge was used as the inoculum for the BMP experiments. Basic characteristics of the wastewater are shown in Table 6.1.

Table 6.1. Characterisation of real wastewater for the FO feed solution (average concentration \pm standard deviation from triplicate measurements).

Parameters		Wastewater
Chemical oxygen demand (COD)	mg/L	288.8 ± 10.7
Total solids (TS)	g/L	0.67 ± 0.02
Volatile solids (VS)	g/L	0.26 ± 0.01

Draw solutions were prepared using either NaCl or NaOAc at 0.65M and 0.72M, respectively. These concentrations were obtained from OLI Stream Analyzer (OLI Systems, Inc., Morris Plains, New Jersey, USA) calculations to achieve an equivalent osmotic pressure of 30 bar (similar to that of seawater).

BMP experiments were conducted using a synthetic wastewater solution. First a stock solution was prepared to contain 4 g/L glucose, 1 g/L peptone, 0.35 g/L urea, 0.175 g/L KH_2PO_4 , 0.175 g/L MgSO_4 , 0.1 g/L FeSO_4 , and 2.25 g/L NaOAc. This stock solution was

then diluted to accurately simulate the COD of the initial primary effluent and as the COD increases with FO water recovery. Analytical grade NaCl or NaOAc was also added to the synthetic feed to simulate salinity increase corresponding to each water recovery values as calculated from the FO experiments. Pure nitrogen gas was used as the headspace in the BMP bottles and a 1M sodium hydroxide (NaOH) solution was used to absorb the carbon dioxide (CO₂) and hydrogen sulphide (H₂S) from the biogas.

A thin film composite (TFC) FO membrane was used in this study and was supplied by Porifera (Porifera Inc., Hayward, CA). The TFC membrane had a polyamide active layer with a porous polysulfone layer for support.

6.2.2. Forward osmosis system

The lab-scale FO system used in this study consisted of a cross-flow membrane cell with an effective membrane area of 50 cm². The membrane cell consisted of two symmetric flow channel for the feed and draw solution to contact the membrane. Each flow channel had length, width, and height dimensions of 100 mm, 50 mm, and 3 mm, respectively. The flat-sheet membrane was inserted between two rubber gaskets and the two semi-cells made of perspex. The feed and draw solutions were circulated through the membrane cell channels via two variable-speed gear pumps (Micropump, Vancouver, Washington, USA). The pump speed was adjusted to maintain the system cross-flow velocity, and the circulation flow rate was regulated using two rotameters. A diamond shaped spacer with a thickness of 1 mm was positioned within the draw solution flow channel to improve mixing.

The flux dynamics of the system were determined according to the standard procedure described by Cath, et al. [186]. The weight change of the draw solution tank was measured using a digital balance (Mettler-Toledo Inc., Hightstown, New Jersey, USA) to determine the permeate water flux. The osmotic pressure of each draw solution was maintained constant during each FO experiment by controlling the solution conductivity. The draw solution conductivity was continuously measured using a conductivity probe (Cole-Parmer, Vernon Hills, Illinois, USA). A peristaltic pump connected to a controller, dosed highly concentrated stock solution (5 M) into the draw solution as the measured conductivity fell below the specified range at a control accuracy of (± 0.1 mS/cm). This re-concentration system was also placed on the digital balance to ensure accurate flux measurements due to weight changes.

6.2.3. Biochemical methane potential experimental set-up

The biochemical methane potential (BMP) experimental set-up consisted of 16 fermentation bottles (Wiltronics Research, Ballarat, Victoria, Australia) that were filled with 500 mL of digested sludge and 250 mL of the simulated FO-preconcentrate. The fermentation bottles were submerged in a water bath that maintained a temperature of 35.0 ± 0.1 °C (Ratek Instruments, Boronia, Victoria, Australia). Each fermentation bottle was sealed with a rubber bung attached to an S-shaped air lock, and flexible plastic tubing was used to transfer biogas to the collection gallery. The gallery included 16 inverted 1000 mL plastic measuring cylinders, filled with a 1 M NaOH solution. The NaOH solution sequestered the CO₂ and H₂S in the biogas, whilst the CH₄ gas displaced the NaOH inside the cylinder. Daily measurements of CH₄ gas production were recorded.

6.2.4. Experimental protocol

For the FO experiments, real wastewater was used as the feed solution and analytical grade draw solutes were dissolved in DI water at the concentration corresponding to an osmotic pressure of 30 bar. The system water recovery was calculated based on the ratio of the cumulative permeate volume and the initial feed solution volume. The FO system was operated continuously until 90% of water had been recovered from the real wastewater. The initial volume of wastewater was 2 L, corresponding to a total concentrate volume of 0.2 L. The water flux was continuously monitored, whilst the wastewater conductivity, pH, and temperature was frequently measured. At specific time intervals, samples of 10 mL volume were withdrawn from the feed solution for COD analysis to represent the amount of organic matter in solution. The circulation flow rates were maintained at 1 L/min and therefore the cross-flow velocity was equivalent to 16.7 cm/s.

At the conclusion of the experiment, the membrane was flushed at a high cross-flow velocity for 30 minutes. This was achieved by replacing the feed and draw solutes with DI water and doubling the cross-flow velocity. After flushing, fresh wastewater was used as the feed solution to verify the water flux recoverability at the initial conditions.

After experimentally determining the pre-concentrated wastewater characteristics (i.e. COD and salinity), a synthetic wastewater solution and each draw solute was used to simulate the wastewater at various water recovery stages. The COD results from the FO experiment using NaCl was used to represent the COD increase in wastewater as no draw solute interference took place (as is the case with NaOAc). A substrate volume of 250 mL and an

inoculum volume of 500 mL was selected, corresponding to an inoculum/substrate ratio of 2:1. Three water recovery values were selected to represent various stages of the pre-concentration process, namely 50, 80 and 90%. The synthetic wastewater solution described in Section 6.2.1 was diluted according to the COD value at each water recovery. Next, the measured conductivity was taken as the total required salinity, and the salinity contribution from the wastewater was calculated. The remaining salinity was assumed to be made up of the reverse solute flux contribution, therefore, the correct amount of concentrated draw solute stock was added to the substrate solution.

For the BMP experiments, the synthetic FO pre-concentrate was prepared and then mixed with 500 mL of digested sludge. A reference condition was used to present the methane production of the inoculum, and real wastewater was also used in a separate condition for comparison to the synthetic wastewater. The fermentation bottles were purged with nitrogen gas, sealed, and submerged in the water bath. The contents of each bottle was characterised before and after the BMP experiment in terms of pH, conductivity, and COD.

6.2.5. Analytical methods

Standard methods were used during the analysis of basic water quality parameters. The temperature, pH, and electrical conductivity were monitored using an Orion 4-Star pH/conductivity meter (Thermo Scientific, Waltham, MA). COD samples were analysed using a Hach DBR200 COD Reactor and Hatch DR/2000 spectrophotometer (program number 435 COD HR) following the US-EPA Standard Method 5220 D. Total solids (TS) and volatile solids (VS) of the primary effluent were determined within 3 days after sample collection. All samples were stored at 4 °C.

6.3. Results and discussion

6.3.1. Pre-concentration performance using thin film composite membrane

Pre-concentrating wastewater using TFC FO membrane resulted in the substantial increase in COD (i.e. approximately eight-fold) at a water recovery of 90% (Figure 6.1). The COD concentration behaviour of the TFC membrane was very similar to that of the cellulose triacetate (CTA) membrane used in Chapter 4, despite the differences in operating conditions (i.e. hydrodynamic conditions and experimental duration). As no fouling mitigation strategy was implemented for this experiment, it is possible that surface deposition of organics was an important fouling mechanism, and resulted in a lower bulk COD concentration than theoretically possible (i.e. ten-fold). In practice, the fouling layer can be re-suspended into the

feed solution during membrane cleaning, and thus contribute to the feed COD amount. The results shown in Figure 6.1 represent the increase in wastewater COD due to organic matter enrichment, as the NaCl draw solute would not have contributed to wastewater COD, as is the case for NaOAc.

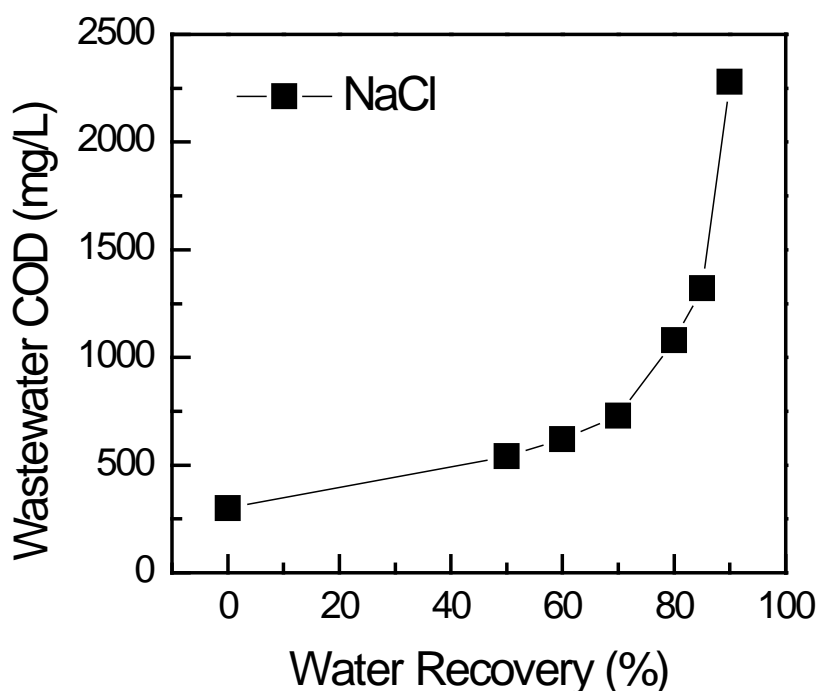


Figure 6.1. Pre-concentration of wastewater COD using NaCl draw solution and TFC FO membrane. Experimental conditions: primary effluent feed solution (2 L); $\pi = 30$ bar draw solution; cross-flow rates of both feed and draw solutions were 1 L/min (corresponding to a cross-flow velocity of 16.7 cm/s).

Similar to the enrichment of COD in pre-concentrated wastewater, the level of salinity also increased as the FO experiment progressed (Figure 6.2). Wastewater conductivity increased for two reasons. Firstly, the natural salinity of the wastewater (i.e. 1 mS/cm) was enriched in the feed solution due to membrane solute rejection. Also, the reverse diffusion of the draw solutes into the feed solution contributed to salinity build-up. As shown in Figure 6.2, the extent of salinity accumulation using NaOAc was 50% lower when compared to NaCl. This result is in good agreement with previous studies, whereby NaOAc has a smaller reverse solute flux due to the lower diffusion properties and large size compared with NaCl [55, 134, 156]. It is important to note that these results cannot be directly compared with those found in Chapter 4 using the CTA membrane, due to the difference in operating conditions. However, it is interesting to note that the TFC membrane using NaCl produced a concentrated wastewater with a larger salinity of approximately 17 mS/cm, compared with

the 13 mS/cm reported using the CTA membrane in Section 4.3.2. This result highlights the significant effects of FO operating conditions on process performance, namely, membrane type, hydrodynamic conditions, and experiment duration.

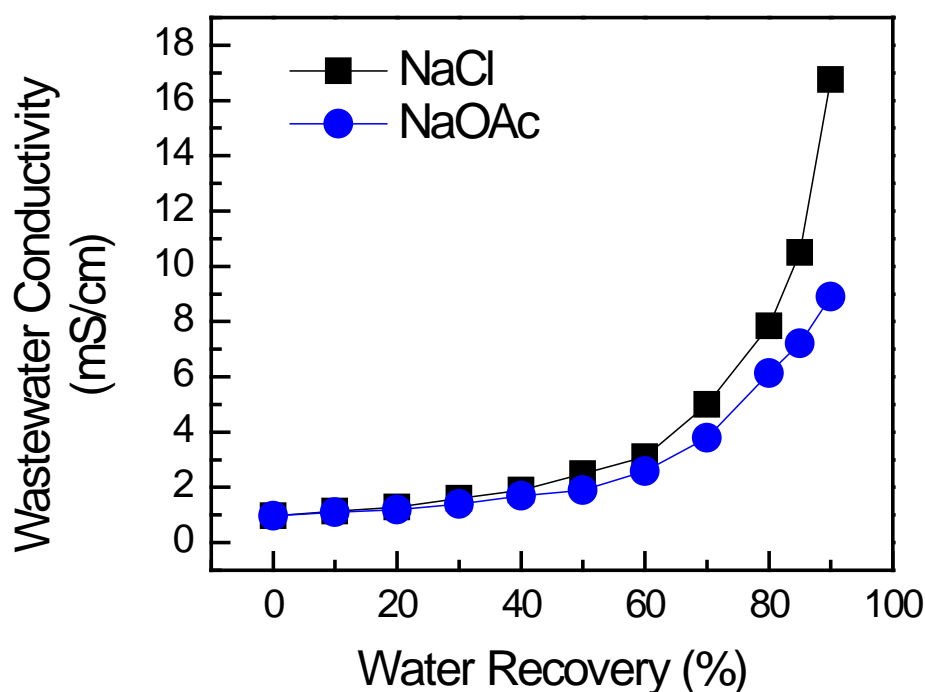


Figure 6.2. Variation in wastewater conductivity for NaCl and NaOAc draw solutions. Experimental conditions as in Figure 6.1.

6.3.2. Effect of forward osmosis concentration factor on methane production

The variation in wastewater characteristics at FO water recoveries of 50, 80, and 90% were simulated in batch anaerobic BMP experiments (Table 6.2). For both draw solutions, the conditions were simulated based on the experimentally determined values for salt concentration (i.e. conductivity) and organic content (i.e. COD) during the FO wastewater pre-concentration experiments. Wastewater COD was simulated using synthetic wastewater and the remaining conductivity requirement was supplied with the relevant amount of each draw solute (i.e. NaCl or NaOAc) as described in Section 6.2.4. As shown in Figure 6.1 and Figure 6.2, increasing water recovery results in an increase in conductivity and COD. However, conductivity and COD have independent and opposing effects on methane production [24]. Increased COD loading in this range (up to 1,000 mg/L) significantly benefit the anaerobic process in terms of methane conversion. Conversely, high conductivity solutions can seriously impact methanogenic health and inhibit methane production.

Table 6.2. Variation in wastewater conductivity and COD simulated in BMP experiments for NaCl and NaOAc. The calculated total COD in each BMP bottle is also shown. Two BMP experiments were performed and each condition was conducted in duplicate.

Substrate	FO water recovery (%)	Wastewater conductivity ($\mu\text{S}/\text{cm}$)	Wastewater COD (mg/L)	Total COD in 750 mL bottle (mg)
Reference	-	-	-	4,000
Real wastewater	0	-	288	4,072
Synthetic wastewater + NaCl	50	2,449	540	4,135
	80	7,846	1,079	4,270
	90	16,750	2,280	4,570
Synthetic wastewater + NaOAc	50	1,889	540	4,675
	80	6,122	1,079	6,306
	90	8,900	2,280	7,588

The cumulative methane production over a period of 30 days demonstrates the varying effect of FO water recovery and draw solute selection on the digestibility of pre-concentrated wastewater (Figure 6.3). Firstly, the methane production of real wastewater was only slightly higher than the reference condition and can be attributed to marginal difference in total COD for these two conditions, as well as due to variations in the inoculum characteristics (Table 6.2). This result highlights the difficulties associated with digesting low strength wastewaters for the purpose of biogas recovery. In all cases, pre-concentration wastewater using FO improved the total wastewater COD, thus tended to increase methane production over the evaluation period. For both NaCl (Figure 6.3A) and NaOAc (Figure 6.3B), the cumulative methane production increased as the system water recovery was maximised. Overall, discernible effect of reverse draw solute flux on methane production was observed, possibly due to the presence of sufficient biodegradable matter in the pre-concentrated wastewater, or because of the applied inoculum/ substrate ratio of 2:1, which may have masked the total salinity.

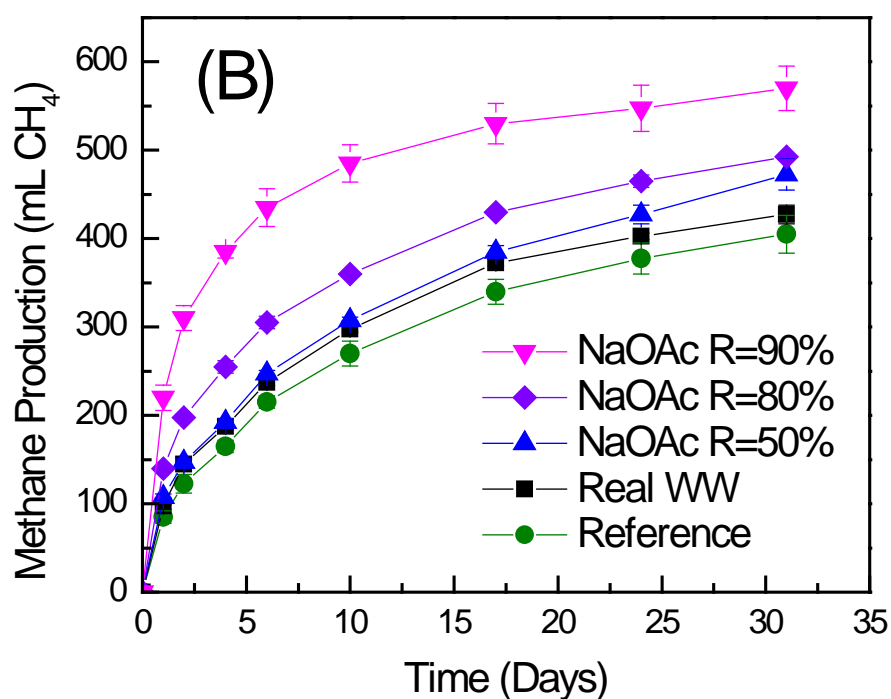
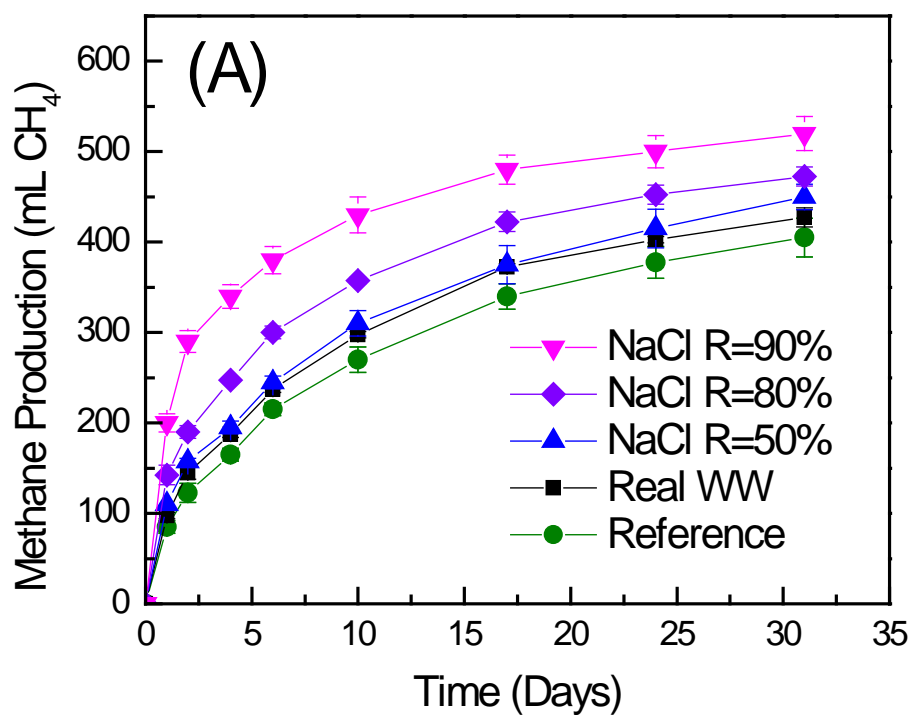


Figure 6.3. Average cumulative methane production over the 30 day evaluation period at various wastewater (WW) pre-concentration stages using (A) NaCl and (B) NaOAc FO draw solutions. Error bars represent n=4 measurements, with two BMP experiments and each condition being performed in duplicate.

The total methane production at various water recovery values and indicates the improvement in digester performance, owing to FO pre-concentration (Figure 6.4). The relative improvement in methane production for NaCl and NaOAc at 90% water recovery was 18 and 25%, respectively. When comparing this process to the direct digestion of raw wastewater, other advantages of using FO to pre-concentrate wastewater include a substantially reduce volumetric digester loading (i.e. 10% of initial wastewater volume) and the provision of a foulant-free draw solution for a subsequent desalination process to recover fresh water. Comparing the two draw solutions, at a water recovery value of 50% and 80%, the methane production of NaOAc exhibited a slightly higher methane production, due to the marginal differences in pre-concentrated wastewater characteristics. However, for 90% water recovery, NaOAc tended to produce a larger amount of methane compared with NaCl, due to the higher contribution of degradable reverse solute flux. Thus, in terms of wastewater pre-concentrate digestibility, no critical concentration factor was found for both draw solutes under these conditions (i.e. 90% water recovery and inoculum/ substrate ratio of 2:1). Although FO reverse solute flux of inorganic draw solutions is reported to negatively affect anaerobic treatment [240], these results show that careful selection of FO operating parameters and digester loadings could potentially improve the process performance. In effect, there is evidence to suggest that further maximising water recovery may not be detrimental to digester health, even when NaCl is used as the draw solution.

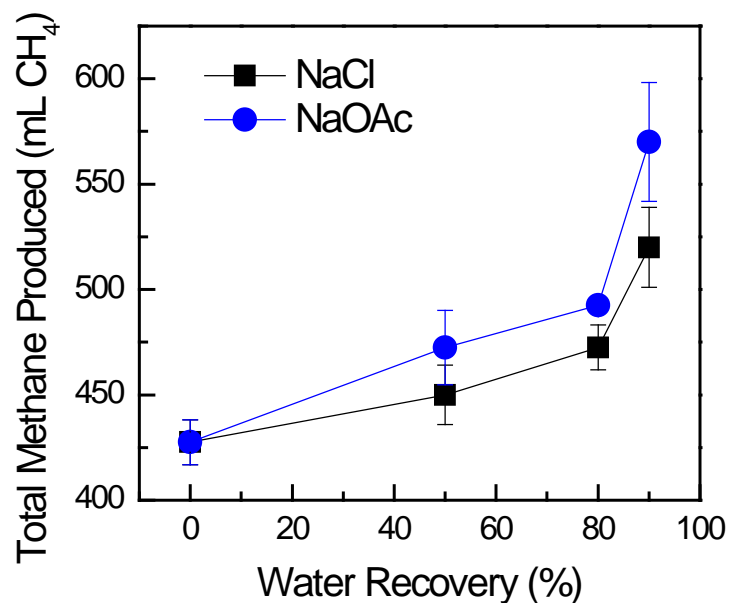


Figure 6.4. Total methane production indicating no critical concentration factor existed up to 90% water recovery. Experimental conditions as in Figure 6.3.

6.3.3. Water flux decline and flux recoverability

The results presented in this chapter show that the rate of membrane fouling using the TFC membrane was higher compared with the CTA membrane used in Chapter 4. This can mostly be attributed to the significantly larger initial water flux of the TFC membrane. Figure 6.5 presents the water flux decline for NaCl and NaOAc at the same osmotic pressure. Although the initial flux of NaOAc was slightly lower than NaCl, both draw solutes exhibited a similar flux decline in the initial stages of the experiment. Subsequently, NaOAc fouling was more severe and indicated the possible interaction between the draw solute and membrane fouling layer [134, 225]. Despite the observed membrane fouling, the complete water flux recovery after physical membrane flushing indicated that no irreversible fouling occurred and that fouling was limited to surface deposition (Figure 6.5).

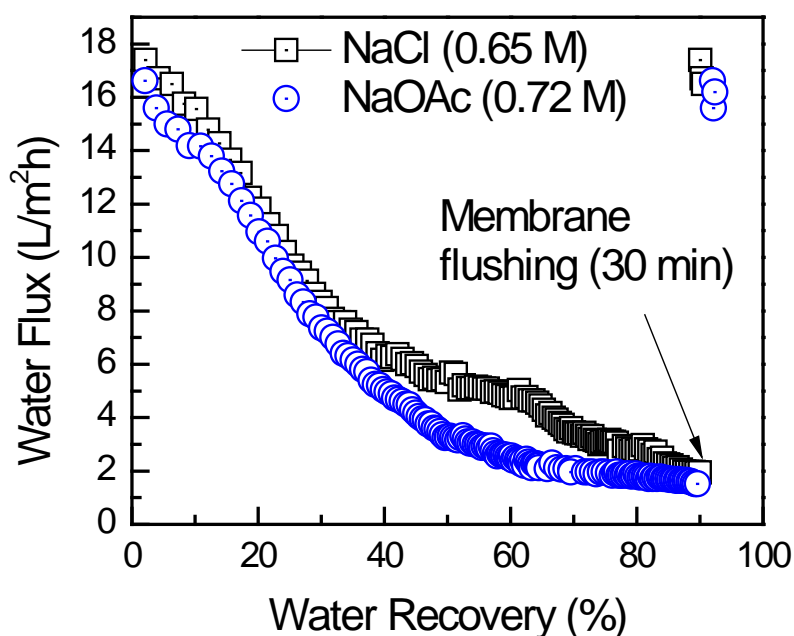


Figure 6.5. Water flux decline and recoverability during FO pre-concentration using TFC membrane. Membrane flushing was performed for 30 min using DI water as the feed and draw solution at double the experimental cross-flow velocity). Experimental conditions as in Figure 6.2. Experimental duration is equivalent to 65 and 72 hours for NaCl and NaOAc, respectively.

6.4. Conclusions

The performance and challenges associated with an FO system that integrates anaerobic treatment for biogas production were presented in this chapter. Raw wastewater pre-

concentration was effectively demonstrated and a BMP experiments were used to further understand the effect of reverse draw solute flux on anaerobic treatment. In general, the TFC membrane showed a drastic improvement compared to CTA membranes, in terms of the obtainable water flux, which has important implications for the commercialisation of FO technology. Additionally, TFC membrane fouling was limited to surface deposition, thus allowed easy cleaning using simple membrane flushing. The simulation of FO pre-concentrated wastewater provided insight into the combined effects of organic matter and salinity loading on methane production. For both of the draw solutes, at various FO water recovery values, no discernible effect on methane production was observed. Based on this result, no critical concentration factor existed under the selected operating parameters (i.e. up to 90% water recovery and inoculum/substrate ratio of 2:1). Overall, the pre-concentrated wastewater containing NaOAc resulted in a higher methane production to that of NaCl (i.e. by 7%).

CHAPTER 7: Phosphorus recovery from digested sludge centrate using seawater-driven forward osmosis

Corresponding publication:

A.J. Ansari, F.I. Hai, W.E. Price and L.D. Nghiem, Phosphorus recovery from digested sludge centrate using seawater-driven forward osmosis, Separation and Purification Technology, 163 (2016), 1-7.

7.1. Introduction

Phosphorus is a key element for all life on earth. Without the phosphorus in biological molecules such as ATP (or adenosine triphosphate) and DNA (or deoxyribonucleic acid), life would not be possible. Phosphorus can also be found in the minerals within bones and teeth. Thus, phosphorus is an essential part of the human diet and a vital element for plants. Indeed, food security is increasingly dependent on the availability of phosphate fertilisers. As natural phosphorus reserves continue to deplete, it is necessary to improve resource efficiency by investing in the recycling and recovery of phosphorus [247]. A considerable fraction of the phosphorus consumed by society ends up in municipal wastewater. In wastewater, phosphorus is a pollutant. When discharged to the environment, phosphorus can cause the widespread eutrophication of receiving waters. This has motivated the implementation of regulatory standards for phosphorus removal at wastewater treatment plants (WWTPs). Overall, the environmental and regulatory need for phosphorus removal, together with the non-renewable nature of phosphorus, give significant incentive for the wastewater treatment sector to recover phosphorus from wastewater [3-5].

A pragmatic option to supplement phosphorus resources is to recover it from wastewater, or more precisely from anaerobically digested sludge centrate. In a typical WWTP, influent phosphorus is biologically accumulated in sludge. When sludge is anaerobically digested, orthophosphate is released and remains dissolved in the sludge centrate (i.e. supernatant). Digested sludge centrate can contain phosphate concentrations in the range of 75–300 mg/L, compared with about 8 mg/L present in influent wastewater [3]. The elevated phosphate concentration in digested sludge centrate presents significant opportunities for phosphorus recovery techniques to be readily integrated into current wastewater treatment infrastructure. Implementing phosphorus recovery can improve nutrient management at WWTPs. Nutrient rich digested sludge centrate is commonly returned to the head of the treatment plant, leading

to the gradual build-up of phosphorus in the plant, decreasing the efficiency of wastewater treatment with respect to phosphorus removal [217]. More importantly, the build-up of phosphorus can also result in gradual struvite precipitation causing blockages and equipment scaling [216]. Thus, by recovering phosphorus from digested sludge centrate, phosphorus removal to comply with effluent discharge standards can be improved and costly maintenance due to blockages can be avoided. At the same time, phosphorus fertilisers can be produced.

Despite the benefits of phosphorus recovery from digested sludge centrate, there are several challenges to developing techniques that are both economically viable and environmentally friendly. Conventional techniques to precipitate agronomically suitable phosphate minerals are expensive and chemically intensive. For example, controlled precipitation of the slow-release fertiliser struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) requires the addition of magnesium in a significant quantity to exceed the stoichiometric ratio. The high cost of magnesium salts makes the conventional struvite recovery process uneconomical and consumes more resources than are produced [248]. Indeed, the primary drivers for most recently installed plants are to prevent struvite blockages and to enhance phosphorus removal. Calcium phosphate precipitates have gained recent attention as an alternative phosphate mineral to be recovered from wastewater, attributed to the simplicity, lower cost and easy acceptance into industrial fertiliser production [249]. Additionally, the initial phosphate concentration is the most important parameter that dictates the efficiency, thus cost effectiveness of a phosphorus recovery process. Therefore, phosphorus recovery can also be enhanced by firstly pre-concentrating the phosphate in digested sludge centrate [152, 250].

Pre-concentrating phosphate in digested sludge centrate can increase the precipitation kinetics of phosphorus mineral recovery. There have been several membrane-based techniques (e.g. membrane distillation and reverse osmosis) for mineral pre-concentration and subsequent recovery from saline industrial wastewaters [251, 252]. However, most of them are not suitable for digested sludge centrate given its high fouling propensity. One key technology with significant potential to perform this function is the osmotically driven membrane filtration process forward osmosis (FO). FO has a number of advantages when applied for the treatment of complex solutions including digested sludge centrate [30, 152], fracking fluid [79, 220], reverse osmosis brine [253], and landfill leachate [79]. FO membranes can retain more than 97% phosphate in digested sludge centrate [30, 152]. Furthermore, fouling in FO is mostly reversible, even with complex feed solutions [63]. The bi-directional transport phenomenon of FO is another important advantage. This leads to an

increase in pH of the feed solution [152, 207], which is optimal for phosphate mineral precipitation. Additionally, the back diffusion of draw solutes can be utilised, thus, seawater can be applied as a draw solution as a potential additional source of calcium for calcium phosphate precipitation. These key attributes make FO possibly the best process to pre-concentrate digested sludge centrate for subsequent phosphorus recovery.

Recent demonstrations of FO to pre-concentrate nutrients prior to phosphate mineral precipitation have shown excellent potential to lower chemical requirements, increase precipitation kinetics, and improve the efficiency of phosphorus recovery from wastewater [5, 30, 108, 114, 152, 254]. Xie et al. [152] demonstrated struvite recovery from digested sludge centrate using a hybrid forward osmosis – membrane distillation (FO-MD) system with MgCl_2 as the draw solution. In addition to providing favourable conditions for struvite precipitation (i.e. elevated ammonium and orthophosphate concentrations, and an elevated pH), the FO system supplied additional magnesium required for struvite precipitation by reverse draw magnesium flux. However, as noted above, a major drawback with the current approach for phosphorus recovery from digested sludge centrate via struvite precipitation is the need for costly magnesium addition. Furthermore, FO usually requires draw solution regeneration, thus, adding another significant cost component to the overall process.

This chapter demonstrates a novel seawater-driven FO technique to recover phosphorus from digested sludge centrate without any chemical addition and draw solute recovery. In this process, phosphate is retained in the digested sludge centrate by the FO membrane, and water is transferred to the seawater draw solution. The enrichment of phosphate, calcium, and magnesium ions, as well as a slightly alkaline condition in the digested sludge centrate allows phosphate minerals to spontaneously precipitate in the feed solution during the filtration process. This avoids the costs associated with calcium or magnesium addition, as well as pH adjustment – a critical requirement of conventional precipitation processes. In addition, the use of seawater as a draw solution eliminates the need for draw solute regeneration, thus providing an energetically favourable system. The process was evaluated in terms of nutrient pre-concentration efficiency, facilitation of phosphate mineral recovery, water flux dynamics, and membrane fouling.

7.2. Materials and methods

7.2.1. Forward osmosis system

A lab-scale, cross-flow FO membrane system with an effective membrane area of 123.5 cm² was used for all filtration experiments [55]. The FO membrane cell consisted of two symmetric flow channels each with a length, width, and height of 130, 95, and 2 mm, respectively. The feed and draw solutions were circulated through each flow channel by two variable speed gear pumps (Micropump, Vancouver, Washington, USA). Two rotameters regulated the circulation flow rate at 1 L/min, which corresponds to a cross-flow velocity of 9 cm/s. The feed solution reservoir was positioned on a digital balance (Mettler-Toledo Inc., Hightstown, New Jersey, USA) and weight changes were recorded to determine the permeate water flux during experiments.

In comparison to previous chapters, A cellulose triacetate (CTA) membrane with embedded polyester screen support was used in this study, and was acquired from Hydration Technologies Innovation (HTI) (Albany, Oregon, USA). The membrane was operated in FO mode (i.e. active layer facing the feed solution).

7.2.2. Experimental protocol

The FO system was used to process digested sludge centrate until 80% water recovery had been achieved (approximately 3 days). The feed and draw (seawater) solutions had initial volumes of 3 and 10 L, respectively, and the system was operated in a closed loop arrangement. A large draw solution to feed solution volume ratio (i.e. V_{DS}/V_{FS}) was selected to minimise the effects of draw solution dilution, and feed solution concentration (i.e. approach of osmotic equilibrium) on water flux decline during experiments.

Water recovery (Rec) was used to represent the water extraction rate of the FO process for each filtration cycle and is defined by Equation 7.1. This was calculated based on the ratio of the cumulative permeate volume and the initial feed solution volume ($V_{f,0}$). Where A_m is the effective membrane area and J_w is the observed water flux at time t .

$$\text{Rec} = \frac{A_m \int_0^T J_w dt}{V_{f,0}} \quad \text{Equation 7.1}$$

Solution temperature, pH, and electrical conductivity were monitored throughout the duration of experiments. Samples of 20 mL were withdrawn from the feed and draw solutions at specific intervals for analysis. The rejection of nutrients by the FO membrane was calculated according to Equation 7.2 [255]. Where J_n is the solute flux (from feed to draw solution) and $c_{n,f}$ is the average concentration of nutrient in the feed solution.

$$R = 1 - \frac{J_n}{J_w c_{n,f}} \quad \text{Equation 7.2}$$

At the conclusion of the filtration cycle, the accumulated solids in the feed solution were collected by centrifuging the concentrated digested sludge centrate at $5,250 \times g$ at 20°C for 5 minutes. The solids were then dried in a desiccator at room temperature.

Water flux dynamics were investigated by determining the FO membrane water flux recoverability due to changes in solution osmotic pressure as well as due to membrane fouling. Firstly, at the end of the filtration cycle, the membrane was removed from the cell and was flushed with deionised water (DI) to remove the fouling layer. With the same feed and draw solutions, the membrane was returned to the cell and the flux recoverability due to membrane fouling was quantified. Next, to confirm the flux decline due to dilution of the draw solution, the feed solution was replaced with DI water, therefore excluding the feed solution osmotic pressure component. Lastly, the feed and draw solutions were replenished with fresh digested sludge centrate and seawater, and subsequent filtration cycles began. All experiments were conducted in duplicate.

7.2.3. Analytical methods

Key water quality parameters for the digested sludge centrate feed solution and seawater draw solution were measured according to standard methods. Phosphate and ammonia were analysed using Flow Injection Analysis (QuickChem 8500, Lachat, Loveland, CO). An inductively coupled plasma–optical emission spectroscopy (ICP–OES) system (ICP-OES 710, Agilent, Australia) was used to determine cation concentrations in the aqueous phase. Amounts of phosphorus, calcium, magnesium, and potassium in the precipitate were determined by dissolving a known amount of precipitate in HNO_3 (5%) followed by ICP–OES analysis. Total organic carbon (TOC) and total nitrogen (TN) were measured using a TOC/TN analyser (TOC-VCSH, Shimadzu, Kyoto, Japan). Temperature, pH, and electrical

conductivity of solutions were monitored by an Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, Waltham, MA).

The obtained solids were characterised using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) (JOEL JSM-6490LV, Japan).

7.2.4. Digested sludge centrate and seawater

Digested sludge centrate was collected from a dewatering centrifuge at the Wollongong Water Recycling Plant (New South Wales, Australia). Seawater was collected from Wollongong (New South Wales, Australia), and was filtered by 0.5 μm paper filters prior to experiments. Key water quality parameters of the digested sludge centrate and seawater are provided in Table 7.1.

Table 7.1: Key physicochemical properties of digested sludge centrate feed solution (FS) and seawater draw solution (DS) (average \pm standard deviation from triplicate measurements).

Parameters	Digested sludge centrate (FS)	Seawater (DS)
Total solids (g/L)	1.13 \pm 0.01	36.80 \pm 0.23
Electrical conductivity (mS/cm)	5.53 \pm 0.05	53.65 \pm 0.30
Osmotic pressure (as NaCl) (bar)	2.00 \pm 0.02	26.80 \pm 0.20
pH	8.03 \pm 0.28	8.00 \pm 0.01
Total organic carbon (mg/L)	589 \pm 11	-
Total nitrogen (mg/L)	741 \pm 21	-
Phosphate (mg/L)	88 \pm 5	< 0.1
Calcium (mg/L)	63 \pm 5	377 \pm 13
Magnesium (mg/L)	14 \pm 5	1,359 \pm 10
Sodium (mg/L)	92 \pm 4	10,366 \pm 26
Potassium (mg/L)	106 \pm 3	503 \pm 6

7.2.5. Forward osmosis water flux model

Water flux dynamics were predicted using the established water flux model for FO membranes [195]. Specifically, as the FO system was operated in a closed loop, the effects of feed and draw solution osmotic pressure changes were scrutinised. The water flux in FO can be predicted using Equation 7.3, and considers the influence of internal concentration

polarisation (ICP) in FO mode operation (i.e. active layer facing the feed solution) [195]. Here, A is the membrane water permeability coefficient, B is the membrane draw solute permeability, and K_m is the mass transfer coefficient (i.e ratio of draw solute diffusion coefficient, D and membrane structural parameter, S (Equation 7.4)). The osmotic pressure of the feed and draw solutions are represented as π_{FS} and π_{DS} , respectively [186].

$$J_w = K_m \ln \left(\frac{A\pi_{DS} + B}{A\pi_{FS} + J_w + B} \right) \quad \text{Equation 7.3}$$

$$K_m = \frac{D}{S} \quad \text{Equation 7.4}$$

The key membrane transport parameters A , B , and S were determined using the protocol previously described by Cath et al. [186]. Details of the reverse osmosis system and procedure to determine A , B , and S are available elsewhere [206]. The experimentally determined values for A and B were 1.81×10^{-12} m/sPa and 6.94×10^{-8} m/sPa, respectively. The membrane S was 670 μm .

Although the ionic composition of seawater is rather complex, it is dominated mostly by NaCl. Thus, for simplicity, the K_m of NaCl was adopted for calculations as opposed to seawater. OLI Stream Analyzer (OLI Systems, Inc., Morris Plains, New Jersey, USA) was used to determine the relationship between the concentration, conductivity, diffusivity, and osmotic pressure of NaCl. The dissolved salts in the digested sludge feed solution were also assumed to be made up of only NaCl. The filtration process was simulated by considering the effects of the loss or gain of permeate water on feed and draw solution osmotic pressure, thus water flux. In FO, water transport is driven by the osmotic pressure difference between the draw and feed solution. The influence of the bi-directional transport of ions on water flux is negligible. Thus, a simple mass balance of salt (NaCl) can be readily obtained to simulate the water flux and concentration of specific ions as a function of water recovery using Equation 3.1 to Equation 7.4.

7.2.6. Mineral species estimation

Visual MINTEQ (v. 3.0) was used as the chemical equilibrium model to estimate the mineral speciation of precipitates. Input data was based on experimentally determined values.

7.3. Results and discussion

7.3.1. Forward osmosis membrane nutrient rejection

Phosphate rejection was high under all experimental conditions (Figure 7.1A). It is noted that phosphate in the draw solution was below the detection limit, excluding the last measurement at 80% water recovery, which was less than 1 mg/L. The high performance of the CTA-FO membrane can be attributed to the electrostatic repulsion between the negatively charged phosphate ions and the strong negative charge of the membrane at the working solution pH (i.e. between pH of 8.0 and 8.7) [114]. Steric hindrance (size exclusion) was also an important rejection mechanism, since phosphate has a large hydrated radius.

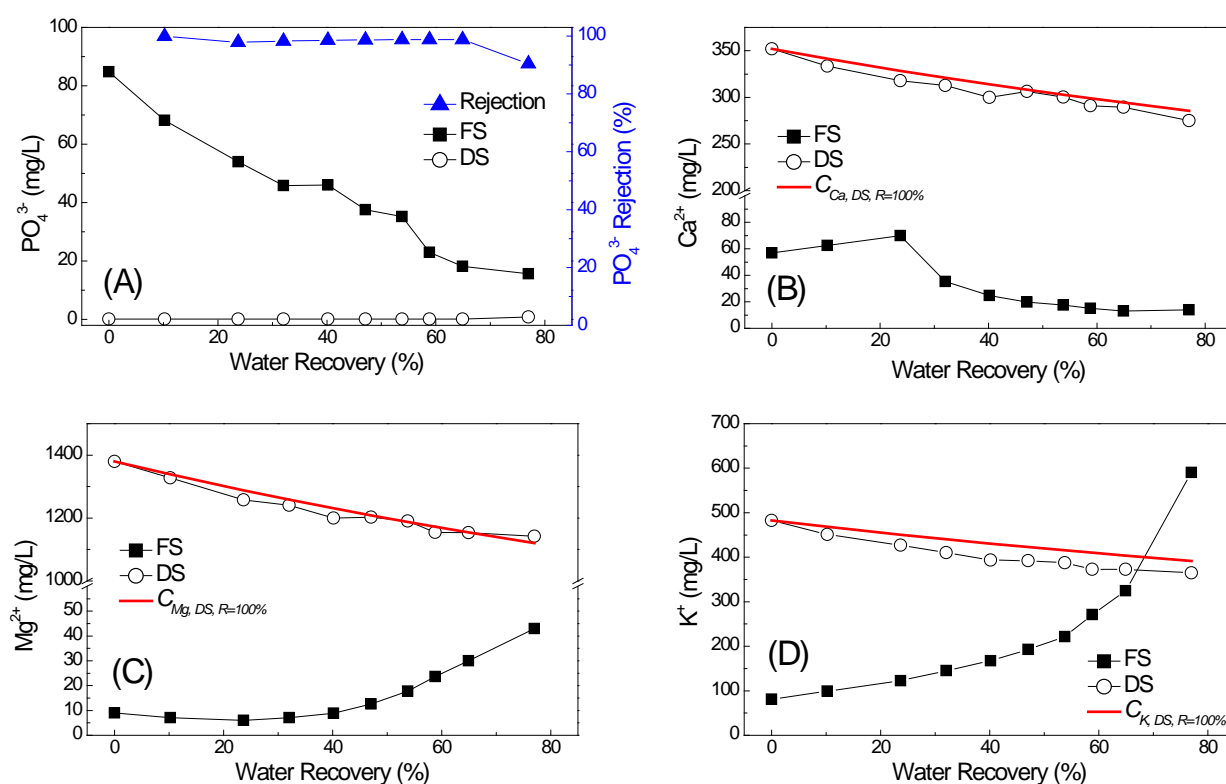


Figure 7.1. Variation of feed solution (FS) and draw solution (DS) concentration, and FO membrane rejection of (A) PO_4^{3-} , (B) Ca^{2+} , (C) Mg^{2+} , and (D) K^+ during FO treatment of digested sludge centrate. The red solid lines ($C_{\text{Ca,DS}}$, $C_{\text{Mg,DS}}$, and $C_{\text{K,DS}}$) are the calculated Ca^{2+} , Mg^{2+} , and K^+ concentration in the draw solution, respectively. All calculations assume that the FO membrane retains 100% of Ca^{2+} , Mg^{2+} , and K^+ .

The FO membrane could also effectively retain calcium, magnesium, and potassium (Figure 7.1B–D). Since the seawater draw solution was allowed to dilute, the ion concentration gradually declined proportionally to the increase in volume. When there is no transfer of calcium and magnesium between the feed (sludge centrate) solution and draw

(seawater) solution, as the draw solution becomes more diluted, their concentrations (i.e. $C_{Ca,DS}$ and $C_{Mg,DS}$) can be calculated by a mass balance. As can be seen in Figure 7.1B and C, the measured concentration of both calcium and magnesium in the draw solution are identical to their calculated values. In other words, calcium and magnesium in the sludge centrate feed were enriched as water was transferred into the draw solution. Results presented in Figure 7.1B and C also infer that reverse permeation of calcium and magnesium in seawater has minimal contribution towards supplementing feed solution concentrations. On the other hand, the experimental concentration of potassium in the draw solution declined at a discernibly faster rate than the calculated value (Figure 7.1D). Results in Figure 7.1D are consistent with the fact that FO membranes are more permeable to monovalent ions (e.g. potassium) than divalent ions (e.g. calcium and magnesium). The reverse permeation of sodium from seawater was also significant. While calcium, magnesium, and potassium can possibly interact with phosphate to form several kinds of phosphorus precipitates, there is no known sodium phosphorus precipitate. Thus, we do not show data related to sodium transport here. Overall, the rejection performance shown in Figure 7.1 suggests that the FO process can effectively pre-concentrate phosphate and other ions in digested sludge centrate.

The high rejection of the FO membrane and the closed loop operation led to the enrichment of phosphate, calcium, magnesium, and potassium in the feed solution. However, an increase in the feed solution concentration could only be observed for magnesium and potassium (Figure 7.1C and D). It appears that under the experimental conditions of this study, magnesium and potassium are not significantly involved in the precipitation of phosphate. Thus, magnesium and potassium concentrations steadily increased due to volume reduction of the feed solution. Magnesium was concentrated approximately by five-fold, in agreement with the rate of volume reduction and confirming the near complete rejection by the FO membrane. As discussed above, potassium enrichment in the feed solution was further augmented by the back diffusion of potassium from the seawater draw solution. It is noteworthy that phosphate and calcium concentrations in the feed sludge centrate did not increase as it was pre-concentrated (Figure 7.1A and B), despite their high rejection by the FO membrane. Phosphate and calcium concentrations in the feed solution decreased overall, suggesting the spontaneous precipitation of calcium phosphate minerals during the filtration process.

7.3.2. Phosphorus removal and recovery

7.3.2.1. Spontaneous precipitation of phosphate minerals

The enrichment of phosphate and calcium in digested sludge centrate by the FO process provides favourable conditions for spontaneous phosphate mineral formation. Throughout the experiment, the mass of phosphate and calcium in the feed solution drastically decreased from their initial values (Figure 7.2). This decline indicates their spontaneous precipitation out of solution, with flaky white solids clearly accumulating at the bottom of the feed solution tank. The mass of phosphate declined at a steady rate from 253 to 10 mg over the course of the experiment. The decline in phosphate coincided with a similar variation in calcium. Initially (i.e. between 0% and 25% water recovery), the mass of calcium in the feed decreased slightly. From 25% onwards, the amount of calcium in the feed decreased gradually and eventually dissipated to below 10 mg. This suggests that the calcium presence actively induced the removal of phosphate through precipitation. The mass of magnesium in the feed solution slightly reduced during the initial stages of the experiment. This could indicate the incorporation of some magnesium into the precipitated solids. However, since the initial and final mass of magnesium in the feed solution is comparable, the uptake of magnesium is likely to be insignificant.

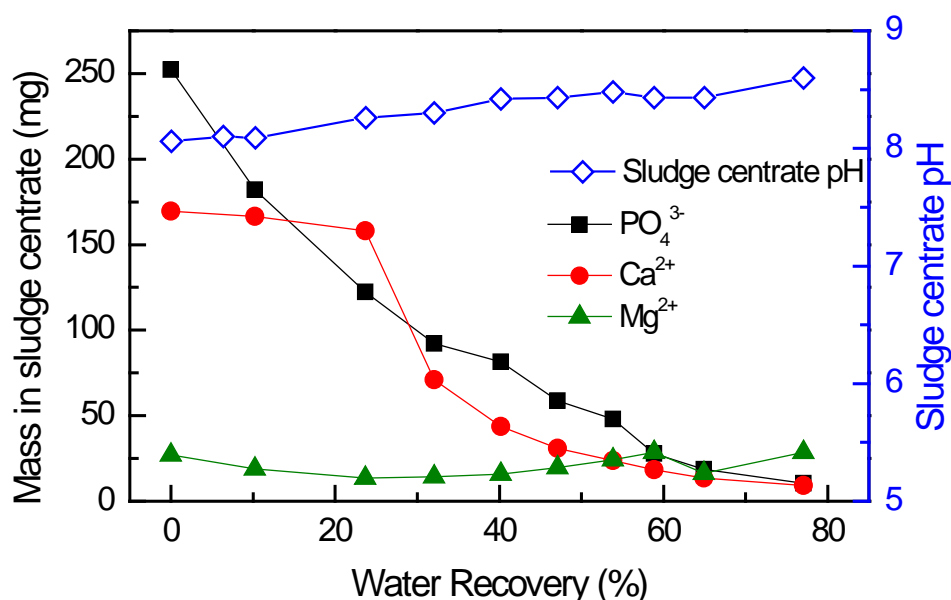


Figure 7.2. Variation of sludge centrate pH and the mass of PO_4^{3-} , Ca^{2+} , and Mg^{2+} in the feed solution during FO treatment of digested sludge centrate.

In addition to the sustained concentrative action of the FO process, the spontaneous precipitation of phosphate minerals was encouraged by the gradual increase in feed solution pH (Figure 7.2). The feed solution pH steadily increased from 8.0 to 8.7 during the experiment due to the diffusion of protons from the feed to the draw solution. This is an inherent phenomenon in FO [207, 256]. Here, the elevated pH further enhances the spontaneous precipitation of phosphate minerals, since calcium phosphate can readily precipitate at a slightly alkaline pH value. Overall, phosphorus removal occurred due to both the concentrative effects from FO membrane water extraction and the increase in the feed solution pH.

The seawater-driven FO process showed an excellent capacity to remove phosphate from digested sludge centrate. The total phosphate removal due to precipitation at the conclusion of the experiment was 92% (Figure 7.3), with only 4% of the initial phosphate content being lost to the draw solution, and 4% remaining in the feed solution. Phosphate removal increased as water recovery increased up to 65% (i.e. concentrated by three-fold). However, when the water recovery increased beyond 65%, phosphate removal reached a plateau value. This can be explained by the deficiency of phosphate and calcium (i.e. both were less than 20 mg/L) in the sludge centrate, thus, lowering the precipitation efficiency from this point onwards.

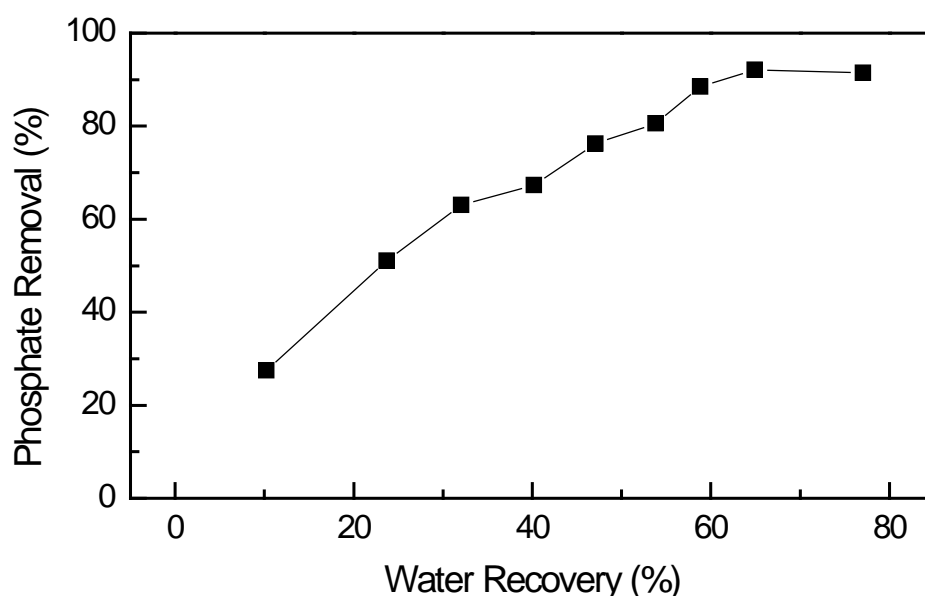


Figure 7.3. Indicative PO_4^{3-} removal by precipitation from digested sludge centrate during seawater-driven FO.

7.3.2.2. Recovered solids

SEM imaging shows a loose arrangement of mineral clusters and EDS analysis confirms that the recovered solids contain phosphorus and calcium (Figure 7.4A and 4B). Calculation of the saturation index (SI) of the initial digested sludge centrate solution using Visual MINTEQ showed the oversaturation of a number of possible calcium phosphate minerals, with hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) displaying the highest potential for precipitation (i.e. $\text{SI} = 13.09$). The increase of the solution pH to 8.7, alongside the five-fold concentration of nutrients in the feed solution, further increased the SI value for hydroxyapatite. Yet, the solids obtained were more likely to consist of amorphous calcium phosphate. This is due to the identification of carbon, oxygen, and magnesium in the solids, and indicates the incorporation of organic matter, as well as the co-precipitation of carbonate and magnesium in the solids [217]. The presence of magnesium [257], carbonate [258], and organic matter [259] was likely to inhibit the formation of hydroxyapatite in the digested sludge centrate. Nonetheless, despite the impact on hydroxyapatite formation, there was no discernible effect on phosphate removal. As can be seen in Figure 7.3, 92% of phosphate in the digested sludge centrate was removed via precipitation.

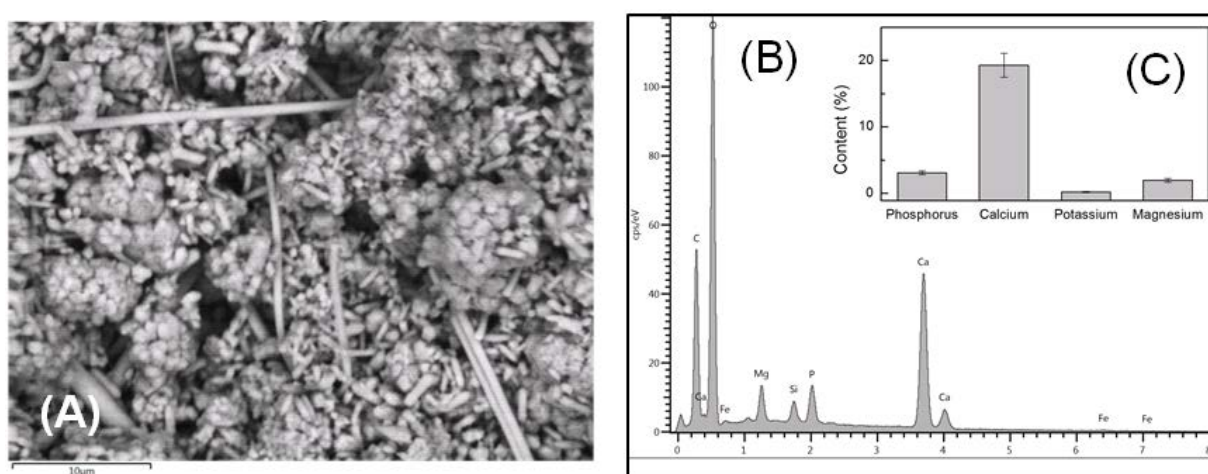


Figure 7.4. (A) Scanning electron microscopic image, (B) energy dispersive X-ray spectrometry spectrum, and (C) elementary composition of the recovered solids (ICP-OES measurement of the precipitate dissolved in acid).

Despite the high phosphorus removal efficiency, elementary analysis (ICP-OES measurement of the precipitate dissolved in acid) of the precipitate obtained revealed that it only contained 3% phosphorus (Figure 7.4C). This gives further evidence that the formation of calcium carbonate was prominent, and is likely to make up a significant portion of the

solids. In other words, the mass percentage of phosphorus in the precipitate is rather small. Given the high carbonate content of digested sludge centrate, additional processing may be required for the production of phosphorus fertilizer from the obtained precipitate. However, the formation of calcium carbonate may have helped to improve the coagulation of phosphate precipitates [260].

7.3.3. Membrane fouling and water flux dynamics

The observed water flux decline in Figure 7.5 was mostly due to the decrease in osmotic pressure, as opposed to membrane fouling. The concentrative action of the feed solution caused an increase in osmotic pressure, whilst the dilution of the draw solution resulted in a decreased osmotic pressure (Figure 7.5). These opposing effects together result in a gradual reduction of the effective osmotic pressure gradient (i.e. driving force) across the FO membrane, and therefore a negative effect on water flux. The feed solution salinity drives the loss of the osmotic driving force, particularly at high water recoveries (>70%) and is attributed to the high initial salinity of digested sludge centrate. As can be seen in Figure 7.5B, the simulated water flux (section 7.2.5) closely resembles the actual flux decline.

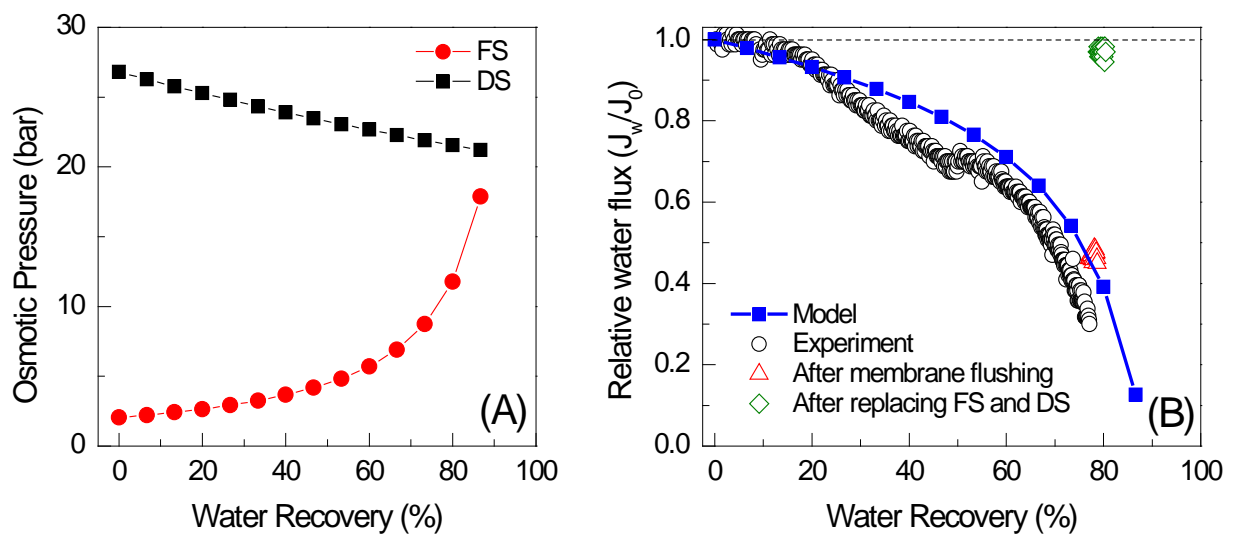


Figure 7.5. (A) Simulated variation of feed solution (FS) and draw solution (DS) osmotic pressure resulting in the reduction of the osmotic driving force during closed-loop FO filtration (FS:DS volume = 3:10 L). (B) Simulated and experimental relative flux decline, with flux recoverability after membrane flushing and after replacing the feed and draw solutions. The experimental water flux was initially 6.4 L/m²h.

Membrane fouling was relatively small and was evidenced in the small difference between the simulated and actual water flux, particularly at high water recovery (Figure

7.5B). Nevertheless, membrane fouling was readily reversible. At 80% water recovery, after simply flushing the membrane surface, the component of flux decline due to membrane fouling was completely recovered. The actual water flux was the same as the simulated value (Figure 7.5B). Furthermore, after replacing the feed and draw solutions with fresh digested sludge centrate and seawater, respectively, the initial water flux of subsequent cycles was also completely restored, thus demonstrating the inherently low fouling propensity of FO. Results reported here are consistent with the literature. Due to absence of any hydraulic pressure and the low applied permeate water flux which allows the fouling layer to be loose and fluid-like, fouling in FO is highly reversible [63]. The reversibility of membrane fouling in our experiment (Figure 7.5B) also confirms that the precipitate occurred in the bulk solution and did not induce scaling on the membrane surface.

7.3.4. Implications

The results presented in this chapter demonstrate that seawater-driven FO can recover phosphorus from digested sludge centrate without any additional chemical requirements and the need for draw solution regeneration. Phosphorus minerals spontaneously precipitate, as the FO membrane pre-concentrates the constituents already present in centrate, as well as elevating the solution pH. The use of seawater as the draw solution may negate the need to apply subsequent desalination processes, and therefore presents an energetically favourable system. The removal of phosphorus from digested sludge centrate also avoids the recycling of nutrients to the head of the treatment plant, thus preventing phosphorus build-up in plants and the associated blockages and equipment scaling. Importantly, the recovered solids containing phosphorus may be utilised as a raw material for phosphate fertiliser production.

During the FO process, a higher water recovery showed to improve phosphate removal from digested sludge centrate, however there is a limitation on the achievable phosphate removal efficiency. In this study, the highest phosphate recovery was achieved when the sludge centrate was pre-concentrated by three-folds. At this point, the effects of osmotic pressure changes on water flux result in only a 30% reduction in the initial water flux. Adopting draw solutions with larger initial osmotic pressures, (i.e. seawater RO brine) is one option to improve system performance in terms of water flux enhancement. Similarly, a draw solution replenishment scheme can be investigated to optimise the trade-offs between the reduction in osmotic pressure due to seawater dilution, accumulation of contaminants in the draw solution, and pumping energy. Nevertheless, the overall restoration of water flux

demonstrates the reversibility of membrane fouling and the suitability of FO to pre-concentrate nutrients in digested sludge centrate.

7.4. Conclusions

In this study, we demonstrate a novel seawater-driven FO process to recover calcium phosphate from digested sludge centrate without any chemical addition and draw solute regeneration. The process was evaluated in terms of nutrient pre-concentration efficiency, facilitation of phosphate mineral recovery, water flux dynamics, and membrane fouling. The FO membrane effectively rejected phosphate and calcium, and led to their enrichment in the digested sludge centrate. The elevated nutrient concentrations and the gradual increase in pH due to the bi-directional transport of protons away from the sludge centrate, improved precipitation kinetics and promoted the spontaneous precipitation of calcium phosphate minerals in the digested sludge centrate. Up to 92% of the initial phosphate was recovered from the digested sludge centrate as amorphous calcium phosphate solids. Membrane fouling did not significantly contribute to water flux decline, and was fully reversible after flushing the membrane with DI water. Overall, seawater driven FO presents a highly energetically favourable option for the sustainable management of digested sludge centrate. Nevertheless, further research is necessary to develop technique to enrich the phosphorus content in the obtained precipitate and to evaluate the economic viability of the proposed process.

CHAPTER 8: Conclusions and Recommendations for Future Work

8.1. Conclusions

The findings from this thesis demonstrate the potential of forward osmosis (FO) as a technological platform to further the development of resource recovery from wastewater. This includes the effectiveness of FO for pre-concentrating the organic matter and nutrients in wastewater for biogas and nutrient recovery. Furthermore FO provides superior pre-treatment for water purification.

A draw solution selection protocol was developed to address the uncertainties associated with the effects of reverse draw solute flux on anaerobic treatment. The biochemical methane potential (BMP) procedure was found to be a reliable screening tool for assessing draw solution compatibility with anaerobic digestion. FO flux performance revealed the strong influence of draw solute physiochemical properties on water and reverse draw solute flux. The solute diffusion coefficient correlated to the extent of internal concentration polarisation for all of the evaluated draw solutes at the same osmotic pressure (i.e. 30 bar). This result indicated the inherent trade-off between selecting draw solutes with a high diffusion coefficient (to maximise water flux) and less mobile draw solutes (to minimise reverse draw solute flux). Sodium acetate (NaOAc) and magnesium acetate displayed unique behaviour, as they displayed acceptable water flux and reverse solute flux selectivity compared to other draw solutes (i.e. inorganic and organic draw solutes). The results of the BMP experiments demonstrated that caution is needed when adopting inorganic draw solutes with a high reverse draw solute flux such as sodium chloride (NaCl). Although NaCl is favourable in terms of water flux, a small but discernible inhibitory effect on methane production was observed. Alternatively, ionic organic draw solutes were suitable due to the acceptable flux performance and the benefits of increased methane production.

The viability of anaerobically digesting low strength water was drastically enhanced by adopting FO pre-concentration. The FO processes consistently concentrated the chemical oxygen demand (COD) of wastewater by approximately eight-fold at a water recovery of 90%. Notably, even low strength wastewater (i.e. COD = 137 mg/L) was pre-concentrated to the COD range suitable for biogas production via anaerobic treatment (i.e. >1,000 mg/L). Using NaCl as the draw solution resulted in a significant accumulation of salinity in the pre-

concentrated wastewater as a result of reverse solute flux and the enrichment of the wastewaters natural salinity. Two alternative draw solutes (i.e. NaOAc and EDTA-2Na) effectively lowered the degree of salinity accumulation in the pre-concentrated wastewater, as both solutes exhibited a low reverse solute flux compared with NaCl. Additionally, the COD of pre-concentrated wastewater was enhanced when using the alternative draw solutes due to the contribution of organics from the reverse solute flux. A continuous flow experiment at a 90% water recovery rate demonstrated the prominence of membrane fouling during direct FO filtration of wastewater. However, optimising the hydrodynamic conditions (i.e. increasing cross-flow velocity) and physical membrane cleaning (water flushing) represented an effective and low impact approach to membrane fouling mitigation.

Membrane fouling is an important issue for FO membranes in applications of resource recovery due to the high suspended solid nature of feed solutions. The developed membrane cleaning protocol effectively utilised physical cleaning methods, rather than intensive chemical strategies. Under accelerated fouling conditions, the fouling associated with the pre-concentration of digested sludge centrate is attributed mostly to the deposition of small mineral crystals and particular matter on the membrane surface. Thus, mitigation by physical cleaning was generally successful. High cross-flow velocity operation and ultrasonication were able to prevent the accumulation of foulants on the membrane during the process. However, air-scouring in the cross-flow configuration was unsuitable due to cake layer compression. In contrast to fouling prevention (i.e. continuous application of control technique during filtration operation), the results show that intermittent membrane cleaning (i.e. temporary suspension of the filtration process for membrane cleaning with water) was more practical. Periodic membrane cleaning using ultrasonication and high cross-flow velocity flushing could restore the initial water flux over several repetitive fouling and cleaning cycles, corresponding to a larger total cumulative water production and a lower cleaning system energy consumption.

The process performance of integrating FO with anaerobic treatment was demonstrated and a number of key challenges identified. The thin film composite (TFC) FO membrane used was found to significantly outperform the cellulose triacetate (CTA) membrane in terms of water flux and ease of cleaning (i.e. fouling reversibility). Regardless of the membrane type, NaOAc significantly lowered the extent of salinity accumulation compared with NaCl. Simulating the pre-concentrated wastewater chemistry for both draw solutes at various FO water recovery values, indicated no discernible effect on methane production. Therefore, no

critical concentration factor existed under the adopted operating parameters (i.e. up to 90% water recovery and inoculum/substrate ratio of 2:1). Generally, the pre-concentrated wastewater containing NaOAc resulted in a higher methane production to that of NaCl. Although it is beyond the scope of this thesis work, it is necessary to also take into account the cost of these draw solutes. The key challenges associated with FO and anaerobic treatment integration include draw solution selection and determining a suitable anaerobic digester hydraulic loading rate.

The technical feasibility of using FO membranes for phosphorus recovery was successfully demonstrated. A novel FO process utilising seawater as the draw solution was used to pre-concentrate phosphorus in digested sludge centrate. The prevailing conditions enabled the recovery of calcium phosphate precipitate without any chemical addition and draw solute regeneration. The substantial phosphate content of digested sludge centrate (85 mg/L) and the high phosphate rejection of the FO membrane (>97%) effectively resulted in the enrichment of phosphate in the feed solution. Other ions, namely calcium, magnesium and potassium that were present in the digested sludge centrate were also enriched equivalent to the FO concentration factor. The bi-directional diffusion of protons away from the digested sludge centrate caused a gradual increase in the feed solution pH during the experiment. The elevated nutrient concentrations and the increased pH promoted the spontaneous precipitation of calcium phosphate minerals in the digested sludge centrate, by improving the precipitation kinetics. Overall, the process resulted in 92% recovery of the initial phosphate amount in the digested sludge centrate. However, the purity of the recovered amorphous calcium phosphate was quite low, containing only 3% phosphorus due to the high carbonate content and presence of competing ions in solution. In terms of FO process performance, the water flux decline was mostly attributed to the osmotic pressure increase of the digested sludge centrate, demonstrated by process modelling. As such, the estimated level of flux decline caused by membrane fouling was found to be fully reversible after simple membrane flushing during the single concentration cycle. Ultrasonication could successfully be applied during long-term operation of the process or at higher water recoveries whereby the effectiveness of flushing will reduce. No draw solute recovery process was required due to the use of a seawater replenishment regime as the draw solution.

8.2. Recommendations for future work

The FO process has a proven capability to achieve simultaneous wastewater treatment and resource recovery. However, the commercialisation and full-scale implementation of FO-based systems requires further extensive research and development. One aspect that deserves attention is the integration of FO with anaerobic treatment. Further insights into the microbial dynamics are warranted, to better understand the influence of salinity on anaerobic digestion and to tailor alternative solutions to improve process performance. Additionally, demonstration of long-term continuous systems is required for the feasible development of the process. The energy dynamics of FO/anaerobic processes are also yet to be comprehensively studied. Evaluation of the system energy production and consumption are necessary to guide future research. Techno-economic assessments that clearly present the advantages of this process compared with current technologies are also required in the form of life cycle analyses which compare FO processes with current technologies.

Further research into the enrichment of phosphorus using FO membranes is also necessary to improve economic viability. Particularly, focus should be placed on the adoption of low-cost and high-salinity draw solutions, such as seawater RO brine. This is due to the limitations on the achievable phosphate removal efficiency due to the osmotic pressure of seawater as found in this thesis. Alternatively, draw solution replenishment regimes for seawater draw solutions should be developed, aiming to optimise the trade-offs between osmotic pressure decreases due to seawater dilution, contaminant accumulation in the draw solution, and pumping energy. Importantly, detailed attention is needed to address the purity and agricultural suitability of the recovered phosphorus using the FO process. Understanding these factors would pave way for research on the economic viability of FO aided nutrient recovery.

References

- [1] G. Amy, N. Ghaffour, Z. Li, L. Francis, R.V. Linares, T. Missimer, S. Lattemann, Membrane-based seawater desalination: Present and future prospects, *Desalination*, 401 (2017) 16-21.
- [2] R. Quentin Grafton, Responding to the 'Wicked Problem' of Water Insecurity, *Water Resources Management*, 31 (2017) 3023-3041.
- [3] E. Desmidt, K. Ghyselbrecht, Y. Zhang, L. Pinoy, B. Van der Bruggen, W. Verstraete, K. Rabaey, B. Meesschaert, Global Phosphorus Scarcity and Full-Scale P-Recovery Techniques: A Review, *Critical Reviews in Environmental Science and Technology*, 45 (2014) 336-384.
- [4] Z. Yuan, S. Pratt, D.J. Batstone, Phosphorus recovery from wastewater through microbial processes, *Current Opinion in Biotechnology*, 23 (2012) 878-883.
- [5] T. Schütte, C. Niewersch, T. Wintgens, S. Yüce, Phosphorus recovery from sewage sludge by nanofiltration in diafiltration mode, *Journal of Membrane Science*, 480 (2015) 74-82.
- [6] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, *Nature*, 452 (2008) 301-310.
- [7] W.W. Mo, Q. Zhang, Energy-nutrients-water nexus: Integrated resource recovery in municipal wastewater treatment plants, *J Environ Manage*, 127 (2013) 255-267.
- [8] H. Hoff, Understanding the Nexus. Background Paper for the Bonn2011 Conference: The Water, Energy and Food Security Nexus, in: Stockholm Environment Institute, Stockholm, 2011.
- [9] W.U.N.W.W.A. Programme), The United Nations World Water Development Report 2014: Water and Energy, in, UNESCO, Paris, 2014.
- [10] WHO/UNICEF, Progress on Sanitation and Drinking Water 2015 update and MDG assessment, (2015).
- [11] A.P. Chanan, S. Vigneswaran, J. Kandasamy, M.A. Johir, Need for a fresh look at phosphorus management in wastewater treatment: Trash to treasure, *Sustainable Environment Research*, 23 (2013) 23-31.
- [12] D. Sedlak, *Water 4.0: The Past, Present, and Future of the World's Most Vital Resource*, Yale University Press, 2014.
- [13] WHO/UNICEF, WASH Post-2015: Proposed targets and indicators for drinking-water, sanitation and hygiene, (2014).
- [14] J. Frijns, J. Hofman, M. Nederlof, The potential of (waste)water as energy carrier, *Energ Convers Manage*, 65 (2013) 357-363.
- [15] W. Verstraete, S.E. Vlaeminck, ZeroWasteWater: short-cycling of wastewater resources for sustainable cities of the future, *Int J Sust Dev World*, 18 (2011) 253-264.
- [16] CSIRO, 3. Are the Economics of Resource Recovery Viable?, (2012).
- [17] M. Molinos-Senante, F. Hernandez-Sancho, R. Sala-Garrido, M. Garrido-Baserba, Economic Feasibility Study for Phosphorus Recovery Processes, *Ambio*, 40 (2011) 408-416.
- [18] WERF, Resource Recovery from Wastewater: A Research Agenda, (2013).
- [19] R. Ordonez, D. Hermosilla, N. Merayo, A. Gasco, C. Negro, A. Blanco, Application of Multi-Barrier Membrane Filtration Technologies to Reclaim Municipal Wastewater for Industrial Use, *Sep Purif Rev*, 43 (2014) 263-310.
- [20] T.Y. Cath, Osmotically and thermally driven membrane processes for enhancement of water recovery in desalination processes, *Desalin Water Treat*, 15 (2010) 279-286.
- [21] S. Salter, *Resources From Waste: A Guide to Integrated Resource Recovery*, (2009).

- [22] P.L. McCarty, J. Bae, J. Kim, Domestic wastewater treatment as a net energy producer-can this be achieved?, *Environmental Science & Technology*, 45 (2011) 7100-7106.
- [23] P.L. McCarty, High-Efficiency Carbon-Neutral Anaerobic Domestic Wastewater Treatment at Any Temperature.
- [24] L. Appels, J. Baeyens, J. Degève, R. Dewil, Principles and potential of the anaerobic digestion of waste-activated sludge, *Progress in Energy and Combustion Science*, 34 (2008) 755-781.
- [25] L.C.S. Lobato, C.A.L. Chernicharo, C.L. Souza, Estimates of methane loss and energy recovery potential in anaerobic reactors treating domestic wastewater, *Water Science and Technology*, 66 (2012) 2745-2753.
- [26] R. Yoo, J. Kim, P.L. McCarty, J. Bae, Anaerobic treatment of municipal wastewater with a staged anaerobic fluidized membrane bioreactor (SAF-MBR) system, *Bioresource Technol*, 120 (2012) 133-139.
- [27] D.J. Batstone, B. Virdis, The role of anaerobic digestion in the emerging energy economy, *Current Opinion in Biotechnology*, 27 (2014) 142-149.
- [28] A.L. Smith, L.B. Stadler, N.G. Love, S.J. Skerlos, L. Raskin, Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: A critical review, *Bioresource Technology*, 122 (2012) 149-159.
- [29] A. Mulder, The quest for sustainable nitrogen removal technologies, in: *Water Science and Technology*, 2003, pp. 67-75.
- [30] R.W. Holloway, A.E. Childress, K.E. Dennett, T.Y. Cath, Forward osmosis for concentration of anaerobic digester centrate, *Water Research*, 41 (2007) 4005-4014.
- [31] C. Sartorius, J. von Horn, F. Tettenborn, Phosphorus Recovery from Wastewater-Expert Survey on Present Use and Future Potential, *Water Environ Res*, 84 (2012) 313-322.
- [32] W. Verstraete, P.V. de Caveye, V. Diamantis, Maximum use of resources present in domestic "used water", *Bioresource Technology*, 100 (2009) 5537-5545.
- [33] T. Tervahauta, T. Hoang, L. Hernández, G. Zeeman, C. Buisman, Prospects of source-separation-based sanitation concepts: A model-based study, *Water (Switzerland)*, 5 (2013) 1006-1035.
- [34] J.J. Bogardi, D. Dudgeon, R. Lawford, E. Flinkerbusch, A. Meyn, C. Pahl-Wostl, K. Vielhauer, C. Vorosmarty, Water security for a planet under pressure: interconnected challenges of a changing world call for sustainable solutions, *Curr Opin Env Sust*, 4 (2012) 35-43.
- [35] W.W. Li, H.Q. Yu, B.E. Rittmann, Chemistry: Reuse water pollutants, *Nature*, 528 (2015) 29-31.
- [36] R.H.E.M. Koppelaar, H.P. Weikard, Assessing phosphate rock depletion and phosphorus recycling options, *Global Environ. Chang.*, 23 (2013) 1454-1466.
- [37] J. Elser, E. Bennett, Phosphorus cycle: A broken biogeochemical cycle, *Nature*, 478 (2011) 29-31.
- [38] G.K. Morse, S.W. Brett, J.A. Guy, J.N. Lester, Review: Phosphorus removal and recovery technologies, *Science of the Total Environment*, 212 (1998) 69-81.
- [39] M. Xie, H.K. Shon, S.R. Gray, M. Elimelech, Membrane-based processes for wastewater nutrient recovery: Technology, challenges, and future direction, *Water Research*, 89 (2016) 210-221.
- [40] Y. Lorenzo-Toja, I. Vázquez-Rowe, M.J. Amores, M. Termes-Rifé, D. Marín-Navarro, M.T. Moreira, G. Feijoo, Benchmarking wastewater treatment plants under an eco-efficiency perspective, *Science of the Total Environment*, 566-567 (2016) 468-479.
- [41] D.L. Sills, V.L. Wade, T.D. DiStefano, Comparative Life Cycle and Technoeconomic Assessment for Energy Recovery from Dilute Wastewater, *Environmental Engineering Science*, 33 (2016) 861-872.

- [42] D.J. Batstone, T. Hülsen, C.M. Mehta, J. Keller, Platforms for energy and nutrient recovery from domestic wastewater: A review, *Chemosphere*, 140 (2015) 2-11.
- [43] H. Gao, Y.D. Scherson, G.F. Wells, Towards energy neutral wastewater treatment: methodology and state of the art, *Environmental Science Process and Impacts*, 16 (2014) 1223-1246.
- [44] M.D. Seib, K.J. Berg, D.H. Zitomer, Low energy anaerobic membrane bioreactor for municipal wastewater treatment, *Journal of Membrane Science*, 514 (2016) 450-457.
- [45] W. Verstraete, S.E. Vlaeminck, ZeroWasteWater: short-cycling of wastewater resources for sustainable cities of the future, *International Journal of Sustainable Development & World Ecology*, 18 (2011) 253-264.
- [46] J. Wan, J. Gu, Q. Zhao, Y. Liu, COD capture: a feasible option towards energy self-sufficient domestic wastewater treatment, *Scientific Reports*, 6 (2016) 25054.
- [47] F.A. Meerburg, N. Boon, T. Van Winckel, J.A.R. Vercamer, I. Nopens, S.E. Vlaeminck, Toward energy-neutral wastewater treatment: A high-rate contact stabilization process to maximally recover sewage organics, *Bioresource Technology*, 179 (2015) 373-381.
- [48] I. Shizas, D. Bagley, Experimental Determination of Energy Content of Unknown Organics in Municipal Wastewater Streams, *Journal of Energy Engineering*, 130 (2004) 45-53.
- [49] W. Luo, F.I. Hai, W.E. Price, W. Guo, H.H. Ngo, K. Yamamoto, L.D. Nghiem, High retention membrane bioreactors: Challenges and opportunities, *Bioresource Technology*, 167 (2014) 539-546.
- [50] M. Xie, J. Lee, L.D. Nghiem, M. Elimelech, Role of pressure in organic fouling in forward osmosis and reverse osmosis, *Journal of Membrane Science*, 493 (2015) 748-754.
- [51] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), *Journal of Membrane Science*, 365 (2010) 34-39.
- [52] A. Achilli, T.Y. Cath, E.A. Marchand, A.E. Childress, The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes, *Desalination*, 239 (2009) 10-21.
- [53] W.C.L. Lay, T.H. Chong, C.Y. Tang, A.G. Fane, J. Zhang, Y. Liu, Fouling propensity of forward osmosis: Investigation of the slower flux decline phenomenon, in: *Water Science & Technology*, 2010, pp. 927-936.
- [54] L. Chen, Y. Gu, C. Cao, J. Zhang, J.-W. Ng, C. Tang, Performance of a submerged anaerobic membrane bioreactor with forward osmosis membrane for low-strength wastewater treatment, *Water Research*, 50 (2014) 114-123.
- [55] A.J. Ansari, F.I. Hai, W. Guo, H.H. Ngo, W.E. Price, L.D. Nghiem, Selection of forward osmosis draw solutes for subsequent integration with anaerobic treatment to facilitate resource recovery from wastewater, *Bioresource Technology*, 191 (2015) 30-36.
- [56] Y. Gu, L. Chen, J.-W. Ng, C. Lee, V.W.C. Chang, C.Y. Tang, Development of anaerobic osmotic membrane bioreactor for low-strength wastewater treatment at mesophilic condition, *Journal of Membrane Science*, 490 (2015) 197-208.
- [57] M.K.Y. Tang, H.Y. Ng, Impacts of different draw solutions on a novel anaerobic forward osmosis membrane bioreactor (AnFOMBR), *Water Science & Technology*, 69 (2014) 2036-2042.
- [58] Y. Kim, L. Chekli, W.-G. Shim, S. Phuntsho, S. Li, N. Ghaffour, T. Leiknes, H.K. Shon, Selection of suitable fertilizer draw solute for a novel fertilizer-drawn forward osmosis-anaerobic membrane bioreactor hybrid system, *Bioresource Technology*, 210 (2016) 26-34.
- [59] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, *Journal of Membrane Science*, 281 (2006) 70-87.
- [60] L. Chekli, S. Phuntsho, J.E. Kim, J. Kim, J.Y. Choi, J.-S. Choi, S. Kim, J.H. Kim, S. Hong, J. Sohn, H.K. Shon, A comprehensive review of hybrid forward osmosis systems:

- Performance, applications and future prospects, *Journal of Membrane Science*, 497 (2016) 430-449.
- [61] K. Lutchmiah, A.R.D. Verliefde, K. Roest, L.C. Rietveld, E.R. Cornelissen, Forward osmosis for application in wastewater treatment: A review, *Water Research*, 58 (2014) 179-197.
- [62] R.W. Holloway, A. Achilli, T.Y. Cath, The osmotic membrane bioreactor: A critical review, *Environmental Science: Water Research and Technology*, 1 (2015) 581-605.
- [63] D.L. Shaffer, J.R. Werber, H. Jaramillo, S. Lin, M. Elimelech, Forward osmosis: Where are we now?, *Desalination*, 356 (2015) 271-284.
- [64] A. Subramani, J.G. Jacangelo, Emerging desalination technologies for water treatment: A critical review, *Water Research*, 75 (2015) 164-187.
- [65] X. Zhang, Z. Ning, D.K. Wang, J.C. Diniz da Costa, Processing municipal wastewaters by forward osmosis using CTA membrane, *Journal of Membrane Science*, 468 (2014) 269-275.
- [66] Z. Wang, J. Zheng, J. Tang, X. Wang, Z. Wu, A pilot-scale forward osmosis membrane system for concentrating low-strength municipal wastewater: performance and implications, *Scientific Reports*, 6 (2016) 21653.
- [67] S.F. Zhao, L. Zou, C.Y.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, *J Membrane Sci*, 396 (2012) 1-21.
- [68] N.Y. Yip, A. Tiraferri, W.A. Phillip, J.D. Schiffman, M. Elimelech, High Performance Thin-Film Composite Forward Osmosis Membrane, *Environmental Science & Technology*, 44 (2010) 3812-3818.
- [69] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, *J Membrane Sci*, 281 (2006) 70-87.
- [70] N.Y. Yip, A. Tiraferri, W.A. Phillip, J.D. Schiffman, M. Elimelech, High performance thin-film composite forward osmosis membrane, *Environmental Science and Technology*, 44 (2010) 3812-3818.
- [71] T.W. Kim, Y. Kim, C. Yun, H. Jang, W. Kim, S. Park, Systematic approach for draw solute selection and optimal system design for forward osmosis desalination, *Desalination*, 284 (2012) 253-260.
- [72] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, *J Membrane Sci*, 364 (2010) 233-241.
- [73] A.D. Wilson, F.F. Stewart, Deriving osmotic pressures of draw solutes used in osmotically driven membrane processes, *J Membrane Sci*, 431 (2013) 205-211.
- [74] L. Chekli, S. Phuntsho, H.K. Shon, S. Vigneswaran, J. Kandasamy, A. Chanan, A review of draw solutes in forward osmosis process and their use in modern applications, *Desalination and Water Treatment*, 43 (2012) 167-184.
- [75] Y. Gao, Y.-N. Wang, W. Li, C.Y. Tang, Characterization of internal and external concentration polarizations during forward osmosis processes, *Desalination*, 338 (2014) 65-73.
- [76] W.A. Phillip, J.S. Yong, M. Elimelech, Reverse Draw Solute Permeation in Forward Osmosis: Modeling and Experiments, *Environ Sci Technol*, 44 (2010) 5170-5176.
- [77] S.A.F. Zhao, L.D. Zou, Relating solution physicochemical properties to internal concentration polarization in forward osmosis, *J Membrane Sci*, 379 (2011) 459-467.
- [78] C. Suh, S. Lee, Modeling reverse draw solute flux in forward osmosis with external concentration polarization in both sides of the draw and feed solution, *J Membrane Sci*, 427 (2013) 365-374.
- [79] B.D. Coday, P. Xu, E.G. Beaudry, J. Herron, K. Lampi, N.T. Hancock, T.Y. Cath, The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams, *Desalination*, 333 (2014) 23-35.

- [80] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents, *Journal of Membrane Science*, 348 (2010) 337-345.
- [81] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, *Journal of Membrane Science*, 320 (2008) 292-302.
- [82] M.M. Motsa, B.B. Mamba, A. D'Haese, E.M.V. Hoek, A.R.D. Verliefde, Organic fouling in forward osmosis membranes: The role of feed solution chemistry and membrane structural properties, *Journal of Membrane Science*, 460 (2014) 99-109.
- [83] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Impact of humic acid fouling on membrane performance and transport of pharmaceutically active compounds in forward osmosis, *Water Research*, 47 (2013) 4567-4575.
- [84] Y. Gu, Y.N. Wang, J. Wei, C.Y. Tang, Organic fouling of thin-film composite polyamide and cellulose triacetate forward osmosis membranes by oppositely charged macromolecules, *Water Research*, 47 (2013) 1867-1874.
- [85] Y. Kim, M. Elimelech, H.K. Shon, S. Hong, Combined organic and colloidal fouling in forward osmosis: Fouling reversibility and the role of applied pressure, *Journal of Membrane Science*, 460 (2014) 206-212.
- [86] E. Arkhangelsky, F. Wicaksana, C. Tang, A.A. Al-Rabiah, S.M. Al-Zahrani, R. Wang, Combined organic-inorganic fouling of forward osmosis hollow fiber membranes, *Water Research*, 46 (2012) 6329-6338.
- [87] M.I. Baoxia, M. Elimelech, Gypsum scaling and cleaning in forward osmosis: Measurements and mechanisms, *Environmental Science and Technology*, 44 (2010) 2022-2028.
- [88] Y. Liu, B. Mi, Effects of organic macromolecular conditioning on gypsum scaling of forward osmosis membranes, *J Membrane Sci*, 450 (2014) 153-161.
- [89] C.-M. Kim, S.-J. Kim, L.H. Kim, M.S. Shin, H.-W. Yu, I.S. Kim, Effects of phosphate limitation in feed water on biofouling in forward osmosis (FO) process, *Desalination*, 349 (2014) 51-59.
- [90] R. Valladares Linares, S.S. Bucs, Z. Li, M. AbuGhdeeb, G. Amy, J.S. Vrouwenvelder, Impact of spacer thickness on biofouling in forward osmosis, *Water Research*, 57 (2014) 223-233.
- [91] H. Yoon, Y. Baek, J. Yu, J. Yoon, Biofouling occurrence process and its control in the forward osmosis, *Desalination*, 325 (2013) 30-36.
- [92] C. Boo, M. Elimelech, S. Hong, Fouling control in a forward osmosis process integrating seawater desalination and wastewater reclamation, *Journal of Membrane Science*, 444 (2013) 148-156.
- [93] Q.C. Ge, M.M. Ling, T.S. Chung, Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future, *J Membrane Sci*, 442 (2013) 225-237.
- [94] M.F.A. Goosen, H. Mahmoudi, N. Ghaffour, Today's and Future Challenges in Applications of Renewable Energy Technologies for Desalination, *Critical Reviews in Environmental Science and Technology*, 44 (2013) 929-999.
- [95] C.H. Tan, H.Y. Ng, A novel hybrid forward osmosis - nanofiltration (FO-NF) process for seawater desalination: Draw solution selection and system configuration, *Desalin Water Treat*, 13 (2010) 356-361.
- [96] J.W. Koo, J.H. Han, T. Yun, S. Lee, J.S. Choi, Integration of forward osmosis with membrane distillation: effect of operating conditions, *Desalination and Water Treatment*, 51 (2013) 5355-5361.
- [97] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, A Forward Osmosis-Membrane Distillation Hybrid Process for Direct Sewer Mining: System Performance and Limitations, *Environmental Science & Technology*, 47 (2013) 13486-13493.

- [98] S. Zhang, P. Wang, X. Fu, T.S. Chung, Sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD), *Water Research*, 52 (2014) 112-121.
- [99] R. Valladares Linares, Z. Li, S. Sarp, S.S. Buco, G. Amy, J.S. Vrouwenvelder, Forward osmosis niches in seawater desalination and wastewater reuse, *Water Research*, 66 (2014) 122-139.
- [100] S. Phuntsho, H.K. Shon, S. Hong, S. Lee, S. Vigneswaran, A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions, *Journal of Membrane Science*, 375 (2011) 172-181.
- [101] S. Phuntsho, H.K. Shon, S. Hong, S. Lee, S. Vigneswaran, J. Kandasamy, Fertiliser drawn forward osmosis desalination: The concept, performance and limitations for fertigation, *Reviews in Environmental Science and Biotechnology*, 11 (2012) 147-168.
- [102] Q. Yang, J. Lei, D.D. Sun, D. Chen, Forward Osmosis Membranes for Water Reclamation, *Separation & Purification Reviews*, 45 (2016) 93-107.
- [103] Q. She, R. Wang, A.G. Fane, C.Y. Tang, Membrane fouling in osmotically driven membrane processes: A review, *Journal of Membrane Science*, 499 (2016) 201-233.
- [104] X. Wang, V.W.C. Chang, C.Y. Tang, Osmotic membrane bioreactor (OMBR) technology for wastewater treatment and reclamation: Advances, challenges, and prospects for the future, *Journal of Membrane Science*, 504 (2016) 113-132.
- [105] E.A. Bell, R.W. Holloway, T.Y. Cath, Evaluation of forward osmosis membrane performance and fouling during long-term osmotic membrane bioreactor study, *Journal of Membrane Science*, 517 (2016) 1-13.
- [106] R.W. Holloway, J. Regnery, L.D. Nghiem, T.Y. Cath, Removal of Trace Organic Chemicals and Performance of a Novel Hybrid Ultrafiltration-Osmotic Membrane Bioreactor, *Environmental Science & Technology*, 48 (2014) 10859-10868.
- [107] W. Luo, F.I. Hai, W.E. Price, W. Guo, H.H. Ngo, K. Yamamoto, L.D. Nghiem, Phosphorus and water recovery by a novel osmotic membrane bioreactor–reverse osmosis system, *Bioresource Technology*, 200 (2016) 297-304.
- [108] G. Qiu, Y.-P. Ting, Direct phosphorus recovery from municipal wastewater via osmotic membrane bioreactor (OMBR) for wastewater treatment, *Bioresource Technology*, 170 (2014) 221-229.
- [109] W.C.L. Lay, Y. Liu, A.G. Fane, Impacts of salinity on the performance of high retention membrane bioreactors for water reclamation: A review, *Water Research*, 44 (2010) 21-40.
- [110] S.H. Park, B. Park, H.K. Shon, S. Kim, Modeling full-scale osmotic membrane bioreactor systems with high sludge retention and low salt concentration factor for wastewater reclamation, *Bioresource Technology*, 190 (2015) 508-515.
- [111] C.-H. Wei, M. Harb, G. Amy, P.-Y. Hong, T. Leiknes, Sustainable organic loading rate and energy recovery potential of mesophilic anaerobic membrane bioreactor for municipal wastewater treatment, *Bioresource Technology*, 166 (2014) 326-334.
- [112] K. Luttmiah, E.R. Cornelissen, D.J.H. Harmsen, J.W. Post, K. Lampi, H. Ramaekers, L.C. Rietveld, K. Roest, Water recovery from sewage using forward osmosis, *Water Science & Technology*, 64 (2011) 1443-1449.
- [113] S. Zou, H. Yuan, A. Childress, Z. He, Energy Consumption by Recirculation: A Missing Parameter When Evaluating Forward Osmosis, *Environmental Science & Technology*, 50 (2016) 6827-6829.
- [114] W. Xue, T. Tobino, F. Nakajima, K. Yamamoto, Seawater-driven forward osmosis for enriching nitrogen and phosphorous in treated municipal wastewater: Effect of membrane properties and feed solution chemistry, *Water Research*, 69 (2015) 120-130.
- [115] X. Wang, Y. Zhao, B. Yuan, Z. Wang, X. Li, Y. Ren, Comparison of biofouling mechanisms between cellulose triacetate (CTA) and thin-film composite (TFC) polyamide

forward osmosis membranes in osmotic membrane bioreactors, *Bioresource Technology*, 202 (2016) 50-58.

[116] G. Qiu, Y.-P. Ting, Osmotic membrane bioreactor for wastewater treatment and the effect of salt accumulation on system performance and microbial community dynamics, *Bioresource Technology*, 150 (2013) 287-297.

[117] R. Valladares Linares, Z. Li, M. Abu-Ghdaib, C.-H. Wei, G. Amy, J.S. Vrouwenvelder, Water harvesting from municipal wastewater via osmotic gradient: An evaluation of process performance, *Journal of Membrane Science*, 447 (2013) 50-56.

[118] J. Zhang, Q. She, V.W.C. Chang, C.Y. Tang, R.D. Webster, Mining Nutrients (N, K, P) from Urban Source-Separated Urine by Forward Osmosis Dewatering, *Environmental Science & Technology*, 48 (2014) 3386-3394.

[119] Y.D. Scherson, S.-G. Woo, C.S. Criddle, Production of Nitrous Oxide From Anaerobic Digester Centrate and Its Use as a Co-oxidant of Biogas to Enhance Energy Recovery, *Environmental Science & Technology*, 48 (2014) 5612-5619.

[120] B.D. Coday, B.G.M. Yaffe, P. Xu, T.Y. Cath, Rejection of Trace Organic Compounds by Forward Osmosis Membranes: A Literature Review, *Environmental Science & Technology*, 48 (2014) 3612-3624.

[121] A.A. Alturki, J.A. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, M. Elimelech, Removal of trace organic contaminants by the forward osmosis process, *Sep Purif Technol*, 103 (2013) 258-266.

[122] K.C. Wijekoon, F.I. Hai, J. Kang, W.E. Price, W. Guo, H.H. Ngo, L.D. Nghiem, The fate of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides during MBR treatment, *Bioresource Technology*, 144 (2013) 247-254.

[123] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, S. Liang, X.C. Wang, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, *Science of the Total Environment*, 473-474 (2014) 619-641.

[124] H. Siegrist, A. Joss, Review on the fate of organic micropollutants in wastewater treatment and water reuse with membranes, *Water Science & Technology*, 66 (2012) 1369-1376.

[125] X. Song, J. McDonald, W.E. Price, S.J. Khan, F.I. Hai, H.H. Ngo, W. Guo, L.D. Nghiem, Effects of salinity build-up on the performance of an anaerobic membrane bioreactor regarding basic water quality parameters and removal of trace organic contaminants, *Bioresource Technology*, 216 (2016) 399-405.

[126] H.T. Nguyen, N.C. Nguyen, S.-S. Chen, H.H. Ngo, W. Guo, C.-W. Li, A new class of draw solutions for minimizing reverse salt flux to improve forward osmosis desalination, *Science of the Total Environment*, 538 (2015) 129-136.

[127] N.C. Nguyen, H.T. Nguyen, S.-S. Chen, H.H. Ngo, W. Guo, W.H. Chan, S.S. Ray, C.-W. Li, H.-T. Hsu, A novel osmosis membrane bioreactor-membrane distillation hybrid system for wastewater treatment and reuse, *Bioresource Technology*, 209 (2016) 8-15.

[128] S. Zhang, P. Wang, X. Fu, T.-S. Chung, Sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD), *Water Research*, 52 (2014) 112-121.

[129] N.C. Nguyen, H.T. Nguyen, S.-T. Ho, S.-S. Chen, H.H. Ngo, W. Guo, S.S. Ray, H.-T. Hsu, Exploring high charge of phosphate as new draw solute in a forward osmosis-membrane distillation hybrid system for concentrating high-nutrient sludge, *Science of the Total Environment*, 557-558 (2016) 44-50.

[130] Y. Zhang, L. Pinoy, B. Meesschaert, B. Van Der Bruggen, A natural driven membrane process for brackish and wastewater treatment: Photovoltaic powered ED and FO hybrid system, *Environmental Science & Technology*, 47 (2013) 10548-10555.

- [131] A. D'Haese, P. Le-Clech, S. Van Nevel, K. Verbeken, E.R. Cornelissen, S.J. Khan, A.R.D. Verliefde, Trace organic solutes in closed-loop forward osmosis applications: Influence of membrane fouling and modeling of solute build-up, *Water Research*, 47 (2013) 5232-5244.
- [132] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, *Journal of Membrane Science*, 396 (2012) 1-21.
- [133] D.L. Shaffer, N.Y. Yip, J. Gilron, M. Elimelech, Seawater desalination for agriculture by integrated forward and reverse osmosis: Improved product water quality for potentially less energy, *Journal of Membrane Science*, 415-416 (2012) 1-8.
- [134] W. Luo, F.I. Hai, W.E. Price, M. Elimelech, L.D. Nghiem, Evaluating ionic organic draw solutes in osmotic membrane bioreactors for water reuse, *Journal of Membrane Science*, 514 (2016) 636-645.
- [135] A.G. Fane, R. Wang, M.X. Hu, Synthetic membranes for water purification: Status and future, *Angewandte Chemie International Edition*, 54 (2015) 3368-3386.
- [136] B. Van Der Bruggen, P. Luis, Forward osmosis: Understanding the hype, *Reviews in Chemical Engineering*, 31 (2015) 1-12.
- [137] M. Khayet, J.A. Sanmartino, M. Essalhi, M.C. García-Payo, N. Hilal, Modeling and optimization of a solar forward osmosis pilot plant by response surface methodology, *Solar Energy*, 137 (2016) 290-302.
- [138] M.D. Warsinger, H.K. Mistry, G.K. Nayar, W.H. Chung, H.J. Lienhard V, Entropy Generation of Desalination Powered by Variable Temperature Waste Heat, *Entropy*, 17 (2015).
- [139] R. Valladares Linares, Z. Li, V. Yangali-Quintanilla, N. Ghaffour, G. Amy, T. Leiknes, J.S. Vrouwenvelder, Life cycle cost of a hybrid forward osmosis – low pressure reverse osmosis system for seawater desalination and wastewater recovery, *Water Research*, 88 (2016) 225-234.
- [140] R.W. Holloway, L. Miller-Robbie, M. Patel, J.R. Stokes, J. Munakata-Marr, J. Dadakis, T.Y. Cath, Life-cycle assessment of two potable water reuse technologies: MF/RO/UV–AOP treatment and hybrid osmotic membrane bioreactors, *Journal of Membrane Science*, 507 (2016) 165-178.
- [141] M. Xie, M. Zheng, P. Cooper, W.E. Price, L.D. Nghiem, M. Elimelech, Osmotic dilution for sustainable greenwall irrigation by liquid fertilizer: Performance and implications, *Journal of Membrane Science*, 494 (2015) 32-38.
- [142] S. Zou, Z. He, Enhancing wastewater reuse by forward osmosis with self-diluted commercial fertilizers as draw solutes, *Water Research*, 99 (2016) 235-243.
- [143] T.Y. Cath, N.T. Hancock, C.D. Lundin, C. Hoppe-Jones, J.E. Drewes, A multi-barrier osmotic dilution process for simultaneous desalination and purification of impaired water, *Journal of Membrane Science*, 362 (2010) 417-426.
- [144] S. Zhao, L. Zou, Relating solution physicochemical properties to internal concentration polarization in forward osmosis, *Journal of Membrane Science*, 379 (2011) 459-467.
- [145] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, *Journal of Membrane Science*, 364 (2010) 233-241.
- [146] D. Xiao, C.Y. Tang, J. Zhang, W.C.L. Lay, R. Wang, A.G. Fane, Modeling salt accumulation in osmotic membrane bioreactors: Implications for FO membrane selection and system operation, *Journal of Membrane Science*, 366 (2011) 314-324.
- [147] W.C.L. Lay, J. Zhang, C. Tang, R. Wang, Y. Liu, A.G. Fane, Factors affecting flux performance of forward osmosis systems, *Journal of Membrane Science*, 394-395 (2012) 151-168.

- [148] M. Galib, E. Elbeshbishy, R. Reid, A. Hussain, H.-S. Lee, Energy-positive food wastewater treatment using an anaerobic membrane bioreactor (AnMBR), *J Environ Manage*, 182 (2016) 477-485.
- [149] Y. Sun, J. Tian, Z. Zhao, W. Shi, D. Liu, F. Cui, Membrane fouling of forward osmosis (FO) membrane for municipal wastewater treatment: A comparison between direct FO and OMBR, *Water Research*, 104 (2016) 330-339.
- [150] W. Luo, M. Xie, F.I. Hai, W.E. Price, L.D. Nghiem, Biodegradation of cellulose triacetate and polyamide forward osmosis membranes in an activated sludge bioreactor: Observations and implications, *Journal of Membrane Science*, 510 (2016) 284-292.
- [151] G. Qiu, Y.-M. Law, S. Das, Y.-P. Ting, Direct and Complete Phosphorus Recovery from Municipal Wastewater Using a Hybrid Microfiltration-Forward Osmosis Membrane Bioreactor Process with Seawater Brine as Draw Solution, *Environmental Science & Technology*, 49 (2015) 6156-6163.
- [152] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Toward Resource Recovery from Wastewater: Extraction of Phosphorus from Digested Sludge Using a Hybrid Forward Osmosis–Membrane Distillation Process, *Environmental Science & Technology Letters*, 1 (2014) 191-195.
- [153] P. Jenicek, J. Bartacek, J. Kutil, J. Zabranska, M. Dohanyos, Potentials and limits of anaerobic digestion of sewage sludge: Energy self-sufficient municipal wastewater treatment plant?, *Water Science & Technology*, 66 (2012) 1277-1281.
- [154] Z.H. Liu, H. Yin, Z. Dang, Y. Liu, Dissolved methane: A hurdle for anaerobic treatment of municipal wastewater, *Environmental Science & Technology*, 48 (2014) 889-890.
- [155] S. Kim, Scale-up of osmotic membrane bioreactors by modeling salt accumulation and draw solution dilution using hollow-fiber membrane characteristics and operation conditions, *Bioresource Technology*, 165 (2014) 88-95.
- [156] K.S. Bowden, A. Achilli, A.E. Childress, Organic ionic salt draw solutions for osmotic membrane bioreactors, *Bioresource Technology*, 122 (2012) 207-216.
- [157] W. Luo, F.I. Hai, J. Kang, W.E. Price, L.D. Nghiem, M. Elimelech, The role of forward osmosis and microfiltration in an integrated osmotic-microfiltration membrane bioreactor system, *Chemosphere*, 136 (2015) 125-132.
- [158] T. Panswad, C. Anan, Impact of high chloride wastewater on an anaerobic/anoxic/aerobic process with and without inoculation of chloride acclimated seeds, *Water Research*, 33 (1999) 1165-1172.
- [159] G. Feijoo, M. Soto, R. Méndez, J.M. Lema, Sodium inhibition in the anaerobic digestion process: Antagonism and adaptation phenomena, *Enzyme and Microbial Technology*, 17 (1995) 180-188.
- [160] O. Lefebvre, R. Moletta, Treatment of organic pollution in industrial saline wastewater: A literature review, *Water Research*, 40 (2006) 3671-3682.
- [161] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, *Journal of Membrane Science*, 320 (2008) 292-302.
- [162] R. Valladares Linares, Z. Li, V. Yangali-Quintanilla, Q. Li, G. Amy, Cleaning protocol for a FO membrane fouled in wastewater reuse, *Desalination and Water Treatment*, 51 (2013) 4821-4824.
- [163] L. Zhang, T.L.G. Hendrickx, C. Kampman, H. Temmink, G. Zeeman, Co-digestion to support low temperature anaerobic pretreatment of municipal sewage in a UASB–digester, *Bioresource Technology*, 148 (2013) 560-566.
- [164] L.D. Nghiem, T.T. Nguyen, P. Manassa, S.K. Fitzgerald, M. Dawson, S. Vierboom, Co-digestion of sewage sludge and crude glycerol for on-demand biogas production, *International Biodeterioration & Biodegradation*, 95, Part A (2014) 160-166.

- [165] Y. Ding, Y. Tian, Z. Li, F. Liu, H. You, Characterization of organic membrane foulants in a forward osmosis membrane bioreactor treating anaerobic membrane bioreactor effluent, *Bioresource Technology*, 167 (2014) 137-143.
- [166] Y. Ding, Y. Tian, J. Liu, N. Li, J. Zhang, W. Zuo, Z. Li, Investigation of microbial structure and composition involved in membrane fouling in the forward osmosis membrane bioreactor treating anaerobic bioreactor effluent, *Chemical Engineering Journal*, 286 (2016) 198-207.
- [167] S. Onoda, Y. Masumori, T. Miyoshi, M. Yasukawa, T. Takahashi, H. Matsuyama, Rejection of nutrients contained in an anaerobic digestion effluent using a forward osmosis membrane, *Desalination and Water Treatment*, 57 (2016) 15748-15758.
- [168] R.W. Holloway, A.S. Wait, A. Fernandes da Silva, J. Herron, M.D. Schutter, K. Lampi, T.Y. Cath, Long-term pilot scale investigation of novel hybrid ultrafiltration-osmotic membrane bioreactors, *Desalination*, 363 (2015) 64-74.
- [169] R.Y. Ning, T.L. Troyer, Colloidal fouling of RO membranes following MF/UF in the reclamation of municipal wastewater, *Desalination*, 208 (2007) 232-237.
- [170] Y.h. Song, D. Donnert, U. Berg, P.G. Weidler, R. Nueesch, Seed selections for crystallization of calcium phosphate for phosphorus recovery, *Journal of Environmental Sciences*, 19 (2007) 591-595.
- [171] J.G. Hering, T.D. Waite, R.G. Luthy, J.E. Drewes, D.L. Sedlak, A Changing Framework for Urban Water Systems, *Environmental Science & Technology*, 47 (2013) 10721-10726.
- [172] N. Cullen, R. Baur, P. Schauer, Three years of operation of North America's first nutrient recovery facility, *Water Science & Technology*, 68 (2013) 763-768.
- [173] B.K. Mayer, L.A. Baker, T.H. Boyer, P. Drechsel, M. Gifford, M.A. Hanjra, P. Parameswaran, J. Stoltzfus, P. Westerhoff, B.E. Rittmann, Total Value of Phosphorus Recovery, *Environmental Science & Technology*, 50 (2016) 6606-6620.
- [174] R. Iranpour, M.K. Stenstrom, G. Tchobanoglous, D. Miller, J. Wright, M. Vossoughi, Environmental engineering: Energy value of replacing waste disposal with resource recovery, *Science*, 285 (1999) 706-711.
- [175] S. Burn, T. Muster, A. Kaksonen, G. Tjandraatmadja, Resource Recovery from Wastewater: A Research Agenda, *Water Environ. Res. Found.*, (2013).
- [176] L.D. Nghiem, P. Manassa, M. Dawson, S.K. Fitzgerald, Oxidation reduction potential as a parameter to regulate micro-oxygen injection into anaerobic digester for reducing hydrogen sulphide concentration in biogas, *Bioresour. Technol.*, 173 (2014) 443-447.
- [177] C. Garcia-Belinchón, C. Garcia-Belinchón, T. Rieck, L. Bouchy, A. Galí, Struvite recovery: Pilot-scale results and economic assessment of different scenarios, *Water Practice Technol.*, 8 (2013) 119-130.
- [178] N.T. Hancock, P. Xu, M.J. Roby, J.D. Gomez, T.Y. Cath, Towards direct potable reuse with forward osmosis: Technical assessment of long-term process performance at the pilot scale, *J. Membr. Sci.*, 445 (2013) 34-46.
- [179] Y. Chen, J.J. Cheng, K.S. Creamer, Inhibition of anaerobic digestion process: A review, *Bioresour. Technol.*, 99 (2008) 4044-4064.
- [180] K. Luttmiah, L. Lauber, K. Roest, D.J.H. Harmsen, J.W. Post, L.C. Rietveld, J.B. van Lier, E.R. Cornelissen, Zwitterions as alternative draw solutions in forward osmosis for application in wastewater reclamation, *Journal of Membrane Science*, 460 (2014) 82-90.
- [181] M.S. Nawaz, G. Gadelha, S.J. Khan, N. Hankins, Microbial toxicity effects of reverse transported draw solute in the forward osmosis membrane bioreactor (FO-MBR), *J. Membr. Sci.*, 429 (2013) 323-329.

- [182] M.K.Y. Tang, H.Y. Ng, Impacts of different draw solutions on a novel anaerobic forward osmosis membrane bioreactor (AnFOMBR), *Water Sci. Technol.*, 69 (2014) 2036-2042.
- [183] K. Koch, B. Helmreich, J.E. Drewes, Co-digestion of food waste in municipal wastewater treatment plants: Effect of different mixtures on methane yield and hydrolysis rate constant, *Appl. Energ.*, 137 (2015) 250-255.
- [184] L.D. Nghiem, T.T. Nguyen, P. Manassa, S.K. Fitzgerald, M. Dawson, S. Vierboom, Co-digestion of sewage sludge and crude glycerol for on-demand biogas production, *Int. Biodeterior. Biodegradation*, (2014).
- [185] F. Mayer, P.A. Gerin, A. Noo, G. Foucart, J. Flammang, S. Lemaigre, G. Sinnaeve, P. Dardenne, P. Delfosse, Assessment of factors influencing the biomethane yield of maize silages, *Bioresour. Technol.*, 153 (2014) 260-268.
- [186] T.Y. Cath, M. Elimelech, J.R. McCutcheon, R.L. McGinnis, A. Achilli, D. Anastasio, A.R. Brady, A.E. Childress, I.V. Farr, N.T. Hancock, J. Lampi, L.D. Nghiem, M. Xie, N.Y. Yip, Standard Methodology for Evaluating Membrane Performance in Osmotically Driven Membrane Processes, *Desalination*, 312 (2013) 31-38.
- [187] A.D. Eaton, M.A.H. Franson, A.P.H. Association, A.W.W. Association, W.E. Federation, Standard Methods for the Examination of Water & Wastewater, American Public Health Association, 2005.
- [188] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, *J. Membr. Sci.*, 364 (2010) 233-241.
- [189] N.T. Hau, S.-S. Chen, N.C. Nguyen, K.Z. Huang, H.H. Ngo, W. Guo, Exploration of EDTA sodium salt as novel draw solution in forward osmosis process for dewatering of high nutrient sludge, *Journal of Membrane Science*, 455 (2014) 305-311.
- [190] J.S. Yong, W.A. Phillip, M. Elimelech, Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes, *J. Membr. Sci.*, 392-393 (2012) 9-17.
- [191] D.R. Lide, H.V. Kehiaian, *CRC Handbook of Thermophysical and Thermochemical Data*, Taylor & Francis, 1994.
- [192] J.S. Yong, W.A. Phillip, M. Elimelech, Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes, *J Membrane Sci*, 392-393 (2012) 9-17.
- [193] W. Hayduk, H. Laudie, Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions, *AIChE Journal*, 20 (1974) 611-615.
- [194] S.A.F. Zhao, L.D. Zou, Relating solution physicochemical properties to internal concentration polarization in forward osmosis, *J. Membr. Sci.*, 379 (2011) 459-467.
- [195] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis, *Journal of Membrane Science*, 284 (2006) 237-247.
- [196] G. Oh, L. Zhang, D. Jahng, Osmoprotectants enhance methane production from the anaerobic digestion of food wastes containing a high content of salt, *J. Chem. Technol. Biotechnol.*, 83 (2008) 1204-1210.
- [197] A. Vintiloiu, M. Boxriker, A. Lemmer, H. Oechsner, T. Jungbluth, E. Mathies, D. Ramhold, Effect of ethylenediaminetetraacetic acid (EDTA) on the bioavailability of trace elements during anaerobic digestion, *Chem. Eng. J.*, 223 (2013) 436-441.
- [198] A. Grobicki, D.C. Stuckey, The role of formate in the anaerobic baffled reactor, *Water Res.*, 23 (1989) 1599-1602.
- [199] J.A. Siles, J. Brekelmans, M.A. Martín, A.F. Chica, A. Martín, Impact of ammonia and sulphate concentration on thermophilic anaerobic digestion, *Bioresour. Technol.*, 101 (2010) 9040-9048.

- [200] A.J. Ansari, F.I. Hai, W.E. Price, L.D. Nghiem, Phosphorus recovery from digested sludge centrate using seawater-driven forward osmosis, *Sep Purif Technol*, 163 (2016) 1-7.
- [201] S.K. Khanal, *Anaerobic Biotechnology for Bioenergy Production: Principles and Applications*, in, 2009, pp. 1-301.
- [202] B. Mi, M. Elimelech, Silica scaling and scaling reversibility in forward osmosis, *Desalination*, 312 (2013) 75-81.
- [203] H.C. Duong, P. Cooper, B. Nelemans, T.Y. Cath, L.D. Nghiem, Evaluating energy consumption of air gap membrane distillation for seawater desalination at pilot scale level, *Sep Purif Technol*, 166 (2016) 55-62.
- [204] S. Onoda, Y. Masumori, T. Miyoshi, M. Yasukawa, T. Takahashi, H. Matsuyama, Rejection of nutrients contained in an anaerobic digestion effluent using a forward osmosis membrane, *Desalin. Water Treat.*, (2015) 1-11.
- [205] M.S. Nawaz, G. Gadelha, S.J. Khan, N. Hankins, Microbial toxicity effects of reverse transported draw solute in the forward osmosis membrane bioreactor (FO-MBR), *Journal of Membrane Science*, 429 (2013) 323-329.
- [206] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Relating rejection of trace organic contaminants to membrane properties in forward osmosis: Measurements, modelling and implications, *Water Research*, 49 (2014) 265-274.
- [207] N.T. Hancock, T.Y. Cath, Solute Coupled Diffusion in Osmotically Driven Membrane Processes, *Environmental Science & Technology*, 43 (2009) 6769-6775.
- [208] G. Calvo, A. Valero, A. Valero, Assessing maximum production peak and resource availability of non-fuel mineral resources: Analyzing the influence of extractable global resources, *Resources, Conservation and Recycling*, 125 (2017) 208-217.
- [209] D. Cordell, J.-O. Drangert, S. White, The story of phosphorus: Global food security and food for thought, *Global Environmental Change*, 19 (2009) 292-305.
- [210] R.W. Scholz, F.W. Wellmer, Approaching a dynamic view on the availability of mineral resources: What we may learn from the case of phosphorus?, *Global Environmental Change*, 23 (2013) 11-27.
- [211] C.M. Lwin, M. Murakami, S. Hashimoto, The implications of allocation scenarios for global phosphorus flow from agriculture and wastewater, *Resources, Conservation and Recycling*, 122 (2017) 94-105.
- [212] O. Krüger, C. Adam, Phosphorus in recycling fertilizers - analytical challenges, *Environmental Research*, 155 (2017) 353-358.
- [213] K.C. van Dijk, J.P. Lesschen, O. Oenema, Phosphorus flows and balances of the European Union Member States, *Science of the Total Environment*, 542, Part B (2016) 1078-1093.
- [214] B. Li, I. Boiarkina, B. Young, W. Yu, Substance flow analysis of phosphorus within New Zealand and comparison with other countries, *Science of the Total Environment*, 527-528 (2015) 483-492.
- [215] N. Martí, R. Barat, A. Seco, L. Pastor, A. Bouzas, Sludge management modeling to enhance P-recovery as struvite in wastewater treatment plants, *J Environ Manage*, 196 (2017) 340-346.
- [216] K.S. Le Corre, E. Valsami-Jones, P. Hobbs, S.A. Parsons, Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review, *Critical Reviews in Environmental Science and Technology*, 39 (2009) 433-477.
- [217] L.E. de-Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003), *Water Research*, 38 (2004) 4222-4246.

- [218] G. Qiu, S. Zhang, D.S. Srinivasa Raghavan, S. Das, Y.-P. Ting, The potential of hybrid forward osmosis membrane bioreactor (FOMBR) processes in achieving high throughput treatment of municipal wastewater with enhanced phosphorus recovery, *Water Research*, 105 (2016) 370-382.
- [219] R. Liu, Y. Wang, G. Wu, J. Luo, S. Wang, Development of a selective electrodialysis for nutrient recovery and desalination during secondary effluent treatment, *Chemical Engineering Journal*, 322 (2017) 224-233.
- [220] X.-M. Li, B. Zhao, Z. Wang, M. Xie, J. Song, L.D. Nghiem, T. He, C. Yang, C. Li, G. Chen, Water reclamation from shale gas drilling flow-back fluid using a novel forward osmosis–vacuum membrane distillation hybrid system, *Water Science & Technology*, 69 (2014) 1036-1044.
- [221] G. Chen, Z. Wang, L.D. Nghiem, X.-M. Li, M. Xie, B. Zhao, M. Zhang, J. Song, T. He, Treatment of shale gas drilling flowback fluids (SGDFs) by forward osmosis: Membrane fouling and mitigation, *Desalination*, 366 (2015) 113-120.
- [222] K.L. Hickenbottom, N.T. Hancock, N.R. Hutchings, E.W. Appleton, E.G. Beaudry, P. Xu, T.Y. Cath, Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations, *Desalination*, 312 (2013) 60-66.
- [223] J. Li, A. Niu, C.-J. Lu, J.-H. Zhang, M. Junaid, P.R. Strauss, P. Xiao, X. Wang, Y.-W. Ren, D.-S. Pei, A novel forward osmosis system in landfill leachate treatment for removing polycyclic aromatic hydrocarbons and for direct fertigation, *Chemosphere*, 168 (2017) 112-121.
- [224] A.J. Ansari, F.I. Hai, W.E. Price, J.E. Drewes, L.D. Nghiem, Forward osmosis as a platform for resource recovery from municipal wastewater - A critical assessment of the literature, *Journal of Membrane Science*, 529 (2017) 195-206.
- [225] Q.H. She, X. Jin, Q.H. Li, C.Y.Y. Tang, Relating reverse and forward solute diffusion to membrane fouling in osmotically driven membrane processes, *Water Research*, 46 (2012) 2478-2486.
- [226] T. Majeed, S. Phuntsho, L. Chekli, S.-H. Lee, K. Kim, H.K. Shon, Role of various physical and chemical techniques for hollow fibre forward osmosis membrane cleaning, *Desalination and Water Treatment*, 57 (2016) 7742-7752.
- [227] N. Nguyen Cong, N. Hau Thi, C. Shiao-Shing, N. Nhat Thien, L. Chi-Wang, Application of forward osmosis (FO) under ultrasonication on sludge thickening of waste activated sludge, *Water Science & Technology*, 72 (2015) 1301-1307.
- [228] Y.-J. Choi, S.-H. Kim, S. Jeong, T.-M. Hwang, Application of ultrasound to mitigate calcium sulfate scaling and colloidal fouling, *Desalination*, 336 (2014) 153-159.
- [229] Z. Wang, J. Tang, C. Zhu, Y. Dong, Q. Wang, Z. Wu, Chemical cleaning protocols for thin film composite (TFC) polyamide forward osmosis membranes used for municipal wastewater treatment, *Journal of Membrane Science*, 475 (2015) 184-192.
- [230] X. Wang, T. Hu, Z. Wang, X. Li, Y. Ren, Permeability recovery of fouled forward osmosis membranes by chemical cleaning during a long-term operation of anaerobic osmotic membrane bioreactors treating low-strength wastewater, *Water Research*, 123 (2017) 505-512.
- [231] B. Mi, M. Elimelech, Gypsum Scaling and Cleaning in Forward Osmosis: Measurements and Mechanisms, *Environmental Science & Technology*, 44 (2010) 2022-2028.
- [232] M.O. Lamminen, H.W. Walker, L.K. Weavers, Mechanisms and factors influencing the ultrasonic cleaning of particle-fouled ceramic membranes, *Journal of Membrane Science*, 237 (2004) 213-223.
- [233] B.S. Chanukya, N.K. Rastogi, Ultrasound assisted forward osmosis concentration of fruit juice and natural colorant, *Ultrasonics Sonochemistry*, 34 (2017) 426-435.

- [234] H. Kim, Y. Lee, M. Elimelech, A. Adout, Y.C. Kim, Experimental Study of Ultrasonic Effects on Flux Enhancement in Forward Osmosis Process, Meeting Abstracts, MA2012-01 (2012) 90.
- [235] W. Luo, F.I. Hai, W.E. Price, L.D. Nghiem, Water extraction from mixed liquor of an aerobic bioreactor by forward osmosis: Membrane fouling and biomass characteristics assessment, *Sep Purif Technol*, 145 (2015) 56-62.
- [236] T. Wang, X. He, Z. Wu, J. Li, Direct observation of flow and bubble behavior in flat sheet modules with a distributor, *RSC Advances*, 7 (2017) 19050-19059.
- [237] D. Puyol, D.J. Batstone, T. Hülsen, S. Astals, M. Peces, J.O. Krömer, Resource Recovery from Wastewater by Biological Technologies: Opportunities, Challenges, and Prospects, *Frontiers in Microbiology*, 7 (2016) 2106.
- [238] Z. Jin, F. Meng, H. Gong, C. Wang, K. Wang, Improved low-carbon-consuming fouling control in long-term membrane-based sewage pre-concentration: The role of enhanced coagulation process and air backflushing in sustainable sewage treatment, *Journal of Membrane Science*, 529 (2017) 252-262.
- [239] Y. Kim, S. Li, L. Chekli, S. Phuntsho, N. Ghaffour, T. Leiknes, H.K. Shon, Influence of fertilizer draw solution properties on the process performance and microbial community structure in a side-stream anaerobic fertilizer-drawn forward osmosis – ultrafiltration bioreactor, *Bioresource Technology*, 240 (2017) 149-156.
- [240] S. Li, Y. Kim, S. Phuntsho, L. Chekli, H.K. Shon, T. Leiknes, N. Ghaffour, Methane production in an anaerobic osmotic membrane bioreactor using forward osmosis: Effect of reverse salt flux, *Bioresource Technology*, 239 (2017) 285-293.
- [241] G. Qiu, S. Zhang, D.S. Srinivasa Raghavan, S. Das, Y.-P. Ting, Towards high throughput biological treatment of municipal wastewater and enhanced phosphorus recovery using a hybrid microfiltration-forward osmosis membrane bioreactor with hydraulic retention time in sub-hour level, *Bioresource Technology*, 219 (2016) 298-310.
- [242] X. Wang, C. Wang, C.Y. Tang, T. Hu, X. Li, Y. Ren, Development of a novel anaerobic membrane bioreactor simultaneously integrating microfiltration and forward osmosis membranes for low-strength wastewater treatment, *Journal of Membrane Science*, 527 (2017) 1-7.
- [243] H. Zhang, W. Jiang, H. Cui, Performance of anaerobic forward osmosis membrane bioreactor coupled with microbial electrolysis cell (AnOMEBR) for energy recovery and membrane fouling alleviation, *Chemical Engineering Journal*, 321 (2017) 375-383.
- [244] Y. Kim, S. Li, L. Chekli, Y.C. Woo, C.-H. Wei, S. Phuntsho, N. Ghaffour, T. Leiknes, H.K. Shon, Assessing the removal of organic micro-pollutants from anaerobic membrane bioreactor effluent by fertilizer-drawn forward osmosis, *Journal of Membrane Science*, 533 (2017) 84-95.
- [245] Y. Wu, X. Wang, M.Q.X. Tay, S. Oh, L. Yang, C. Tang, B. Cao, Metagenomic insights into the influence of salinity and cytostatic drugs on the composition and functional genes of microbial community in forward osmosis anaerobic membrane bioreactors, *Chemical Engineering Journal*, 326 (2017) 462-469.
- [246] S. Onoda, Y. Masumori, T. Miyoshi, M. Yasukawa, T. Takahashi, H. Matsuyama, Evaluation of energy production from municipal wastewater using forward osmosis process and anaerobic membrane bioreactor, *Desalination and Water Treatment*, 65 (2017) 1-10.
- [247] P.J.A. Withers, J.J. Elser, J. Hilton, H. Ohtake, W.J. Schipper, K.C. van Dijk, Greening the global phosphorus cycle: how green chemistry can help achieve planetary P sustainability, *Green Chemistry*, 17 (2015) 2087-2099.
- [248] Z. Bradford-Hartke, J. Lane, P. Lant, G. Leslie, Environmental Benefits and Burdens of Phosphorus Recovery from Municipal Wastewater, *Environmental Science & Technology*, 49 (2015) 8611-8622.

- [249] M. Hermassi, C. Valderrama, J. Dosta, J.L. Cortina, N.H. Batis, Evaluation of hydroxyapatite crystallization in a batch reactor for the valorization of alkaline phosphate concentrates from wastewater treatment plants using calcium chloride, *Chemical Engineering Journal*, 267 (2015) 142-152.
- [250] A.T.K. Tran, Y. Zhang, D. De Corte, J.B. Hannes, W. Ye, P. Mondal, N. Jullok, B. Meesschaert, L. Pinoy, B. Van der Bruggen, P-recovery as calcium phosphate from wastewater using an integrated selectrodialysis/crystallization process, *Journal of Cleaner Production*, (2014).
- [251] A. Ali, C.A. Quist-Jensen, F. Macedonio, E. Drioli, Application of membrane crystallization for minerals' recovery from produced water, *Membranes*, 5 (2015) 772-792.
- [252] C.A. Quist-Jensen, F. Macedonio, E. Drioli, Membrane crystallization for salts recovery from brine—an experimental and theoretical analysis, *Desal. Wat. Treat.*, (2015).
- [253] C. Kazner, S. Jamil, S. Phuntsho, H.K. Shon, T. Wintgens, S. Vigneswaran, Forward osmosis for the treatment of reverse osmosis concentrate from water reclamation: process performance and fouling control, *Water Science & Technology*, 69 (2014) 2431-2437.
- [254] G. Qiu, Y.-M. Law, S. Das, Y.-P. Ting, Direct and Complete Phosphorus Recovery from Municipal Wastewater Using a Hybrid Microfiltration-Forward Osmosis Membrane Bioreactor Process with Seawater Brine as Draw Solution, *Environ. Sci. Technol.*, (2015).
- [255] X. Jin, C.Y. Tang, Y. Gu, Q. She, S. Qi, Boric Acid Permeation in Forward Osmosis Membrane Processes: Modeling, Experiments, and Implications, *Environmental Science & Technology*, 45 (2011) 2323-2330.
- [256] M. Xie, W.E. Price, L.D. Nghiem, Rejection of pharmaceutically active compounds by forward osmosis: Role of solution pH and membrane orientation, *Sep Purif Technol*, 93 (2012) 107-114.
- [257] H. Ding, H. Pan, X. Xu, R. Tang, Toward a Detailed Understanding of Magnesium Ions on Hydroxyapatite Crystallization Inhibition, *Crystal Growth and Design*, 14 (2014) 763-769.
- [258] X. Cao, W. Harris, Carbonate and Magnesium Interactive Effect on Calcium Phosphate Precipitation, *Environmental Science & Technology*, 42 (2008) 436-442.
- [259] Y.-h. Song, H.H. Hahn, E. Hoffmann, P.G. Weidler, Effect of humic substances on the precipitation of calcium phosphate, *Journal of Environmental Sciences*, 18 (2006) 852-857.
- [260] W. Ren, Z. Zhou, L.-M. Jiang, D. Hu, Z. Qiu, H. Wei, L. Wang, A cost-effective method for the treatment of reject water from sludge dewatering process using supernatant from sludge lime stabilization, *Sep Purif Technol*, 142 (2015) 123-128.